

SORBITOL	XYLITOL
GLUCITOL	GLYCEROL
GC - MS	IDENTIFICATION
SEPARATION	ANALYSIS

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Mass spectrometry of alditols as trimethylsilyl derivatives

Göran Petersson

Department of Engineering Chemistry, Chalmers University of Technology,
Göteborg, Sweden

Abstract: The trimethylsilyl ethers of alditols with 3, 4, 5 and 6 carbon atoms were investigated. The mass spectra are unusually clearly correlated with the structures. The predominant fragmentations are cleavages in the carbon chain and rearrangement loss of trimethylsilanol. The spectra are closely related to those of the methyl ethers. A spectrum unambiguously identifies a compound as an alditol and permits the determination of its molecular weight.

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Göran Petersson

Department of Engineering Chemistry, Chalmers University of Technology,
Göteborg, Sweden

MASS spectrometric investigations of acyclic sugar alcohol derivatives have been published for methyl ethers¹ and for acetates.² The spectra of the methyl ethers are characterized by prominent peaks from ions formed by cleavages of a bond in the carbon chain, and ions formed by the loss of methanol from high mass ions. The acetates give characteristic peaks from carbon chain cleavage and from the easy loss of one or more molecules of acetic acid and ketene. Both types of derivatives exhibit extensive fragmentation, and no peaks from molecular ions are obtained. Diastereomers give almost identical spectra. An investigation of a large number of mixed derivatives³ demonstrated differences in the influence of OMe and OAc groups on the fragmentation. OMe groups were found to favour cleavage of adjacent C—C bonds (α -cleavage) with charge retention at the OMe groups.

Ease of preparation and excellent properties for gas chromatography has led to an increased use of trimethylsilyl (TMS) derivatives during the past few years. The present investigation was carried out to examine the possibilities of mass spectrometric structural deductions for alditols using these derivatives, and to obtain a base for investigations of TMS derivatives of carbohydrates with more complex structures. A combined gas chromatograph—mass spectrometer was used.

A fragmentation similar to that of the methyl ethers was anticipated since close fragmentation analogies have been reported for methyl and TMS derivatives of other species including some carbohydrates.⁴ Favoured α -cleavage with charge retention has been shown to permit the determination of the position of trimethylsilyloxy groups in derivatives of acyclic hydroxyl compounds other than alditols including several di- and trihydroxy compounds.⁵⁻⁸

RESULTS AND DISCUSSION

Mass spectra of the TMS ethers of the following alditols were studied: glucitol, mannitol, galactitol, ribitol, arabinitol, xylitol, erythritol, threitol and glycerol. In Fig. 1 the spectra of a series of these derivatives with increasing number of C atoms are given.

The peaks in the upper mass range have been enlarged by the factors given. The spectra show that the molecules are extensively fragmented. No peaks from the

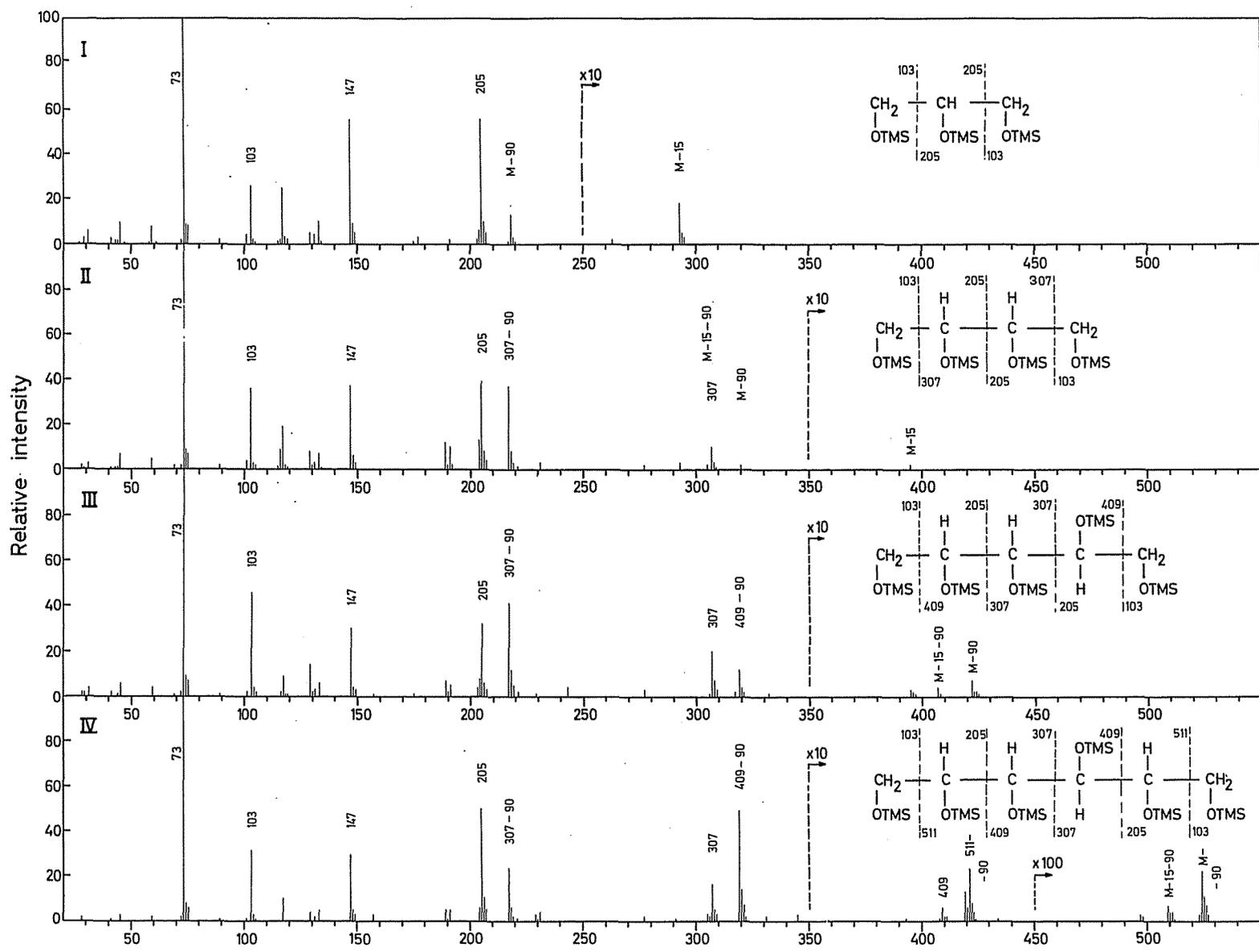


FIG. 1 Mass spectra at 70 eV of the trimethylsilyl ethers of glycerol (I), erythritol (II), arabinitol (III) and glucitol (IV).

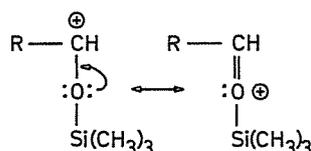
molecular ions (M) were observed and peaks at M-15, commonly encountered for TMS derivatives, were obtained in low intensity for glycerol and the tetritols only.

The peak at $m/e = 73$ from the trimethylsilyl ion is the base peak in all spectra at 70 eV. A prominent peak at $m/e = 147$ was also obtained in all investigated spectra and is characteristic for most compounds with more than one trimethylsiloxy group. The formation of ions with mass 73 and 147 has been discussed in a study of TMS ethers of aliphatic glycols.⁹ They are the two most abundant ions in the spectrum of the ethylene glycol derivative.⁹

The more structure specific peaks were found to be correlated in a very obvious way to the structure, and most of the abundant ions are formed by two main fragmentation modes only, cleavage of the carbon chain and rearrangement loss of trimethylsilanol.

Cleavage of a bond in the carbon chain. As indicated in the structure formulas in Fig. 1, cleavage of C—C bonds gives rise to ions of masses $103 + n \times 102$. Prominent peaks are obtained from most of these ions though their relative intensity gradually decreases above mass 205. The highest member of the series is the M-103 ion. The ethylene glycol derivative gives a prominent peak at $m/e = 103$.⁹

The abundance of these α -cleavage ions is explained by the stabilization of the positive charge by the unshared electron pairs on the O atoms.



The radical fragment formed in the cleavage is stabilized in a similar way. For the alditols this type of resonance stabilization favours cleavage of all C—C bonds, whereas only a few ions from α -cleavage are obtained for monofunctional alcohols and ethers.

The corresponding ions from cleavages in the carbon chain for methyl ethers¹ and acetates² of alditols are accounted for in the same way.

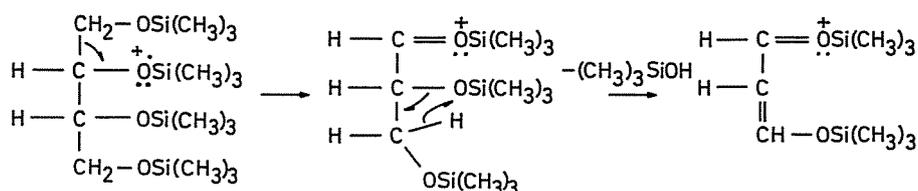
For the TMS derivatives the M-15 ions, arising from the loss of a Me group bonded to silicon, can also be regarded as α -cleavage products.

A peak at $m/e = 103$ is often obtained from rearrangement ions for TMS derivatives of compounds with only secondary hydroxyl groups^{cf. 5} and probably this peak for the alditol derivatives is derived in part from such rearrangement ions. They can be formed favourably by migration of hydrogen to the positively charged C atom in the higher members of the ion series. A metastable peak proves the partial decomposition of the $m/e = 103$ ions to $m/e = 73$ ions by the loss of formaldehyde.^{cf. 9} Formation of the other ions by rearrangement is probably negligible.

Rearrangement loss of trimethylsilanol. Loss of a trimethylsiloxy group together with a hydrogen (90 mu) explains the occurrence of the remaining prominent peaks in the upper mass range of the spectra. Ions with mass M-90 formed from the molecular ions give rise to the peak with the highest mass number for pentitols and hexitols. The relative intensity of this peak increases rapidly with decreasing mol. wt. Abundant ions with a mass 90 units lower than even-electron ions from α -cleavage are obtained

at masses 217 (307-90), 319 (409-90) and 421 (511-90) and at M-15-90. Ions from the loss of two trimethylsilanol molecules are less prominent, but explain the presence of several peaks of low intensity.

A strong metastable peak for tetrityls, pentitols and hexitols corresponds to the decomposition $m/e = 307 \rightarrow m/e = 217$ ($m^* = 153.5-154$; calculated 153.4) and demonstrates that at least part of the ions with mass 217 are formed in fragmentation sequences similar to the following for erythritol. The α -cleavage probably precedes the rearrangement loss for all the fragmentations of this type, but a low abundance of the precursor ion for the loss of trimethylsilanol precludes the presence of distinct metastable peaks in most cases.



The spectra of the methyl ethers of pentitols and hexitols¹ exhibit peaks from the loss of methanol which are very closely related to those from the loss of trimethylsilanol for the TMS ethers with regard to masses and intensities. Loss of ketene and more than one molecule of acetic acid² makes the spectra of the acetates more complex and much different from those of the two types of ether derivatives.

Less prominent fragmentations. Hydrogen abstraction from C-3 and the migration of a trimethylsiloxy radical from C-1 to C-3 with the loss of the fragment containing C-1 and C-2 offers an explanation of the peaks at M-117 which is similar to that given for analogous peaks for the methyl ethers.¹ Most likely 1,3-migration of a trimethylsiloxy radical to the positively charged carbon atom in ions from carbon chain cleavages also explains the formation of ions with mass 191.^{cf. 4}

The odd-electron ions with $m/e = 204$ probably contain two adjacent C atoms with substituents and are formed by the cleavage of two bonds. Expulsion of formaldehyde from the ions with mass 307 ($m^* = 250-250.5$; calc. 249.9) gives a plausible explanation of the peaks at $m/e = 277$. The peaks at $m/e = 231$ for tetrityls, $m/e = 243$ for pentitols and $m/e = 345$ for hexitols can be ascribed to the loss of a trimethylsiloxy group together with one or two trimethylsilanol molecules.

The peaks from these fragmentations for the xylitol derivative are indicated in Fig. 2 by their mass numbers. They are smaller than the peaks from the two main fragmentation modes in the same mass range.

Low electron energy spectra. Spectra at the electron energy 20 eV were measured for representative derivatives with 3, 4, 5, and 6 C atoms in the chain. In Fig. 2 the spectrum of the xylitol derivative is given below that at 70 eV.

The most marked difference is the very low intensity in the spectra at 20 eV of the peaks at $m/e = 73$ and 147, implying formation of the corresponding ions by high energy processes. This makes the more structure specific peaks from carbon chain cleavage and loss of trimethylsilanol still more pronounced and the largest peaks are found among those at $m/e = 205$, 217, 307 and 319. The relative intensity of most

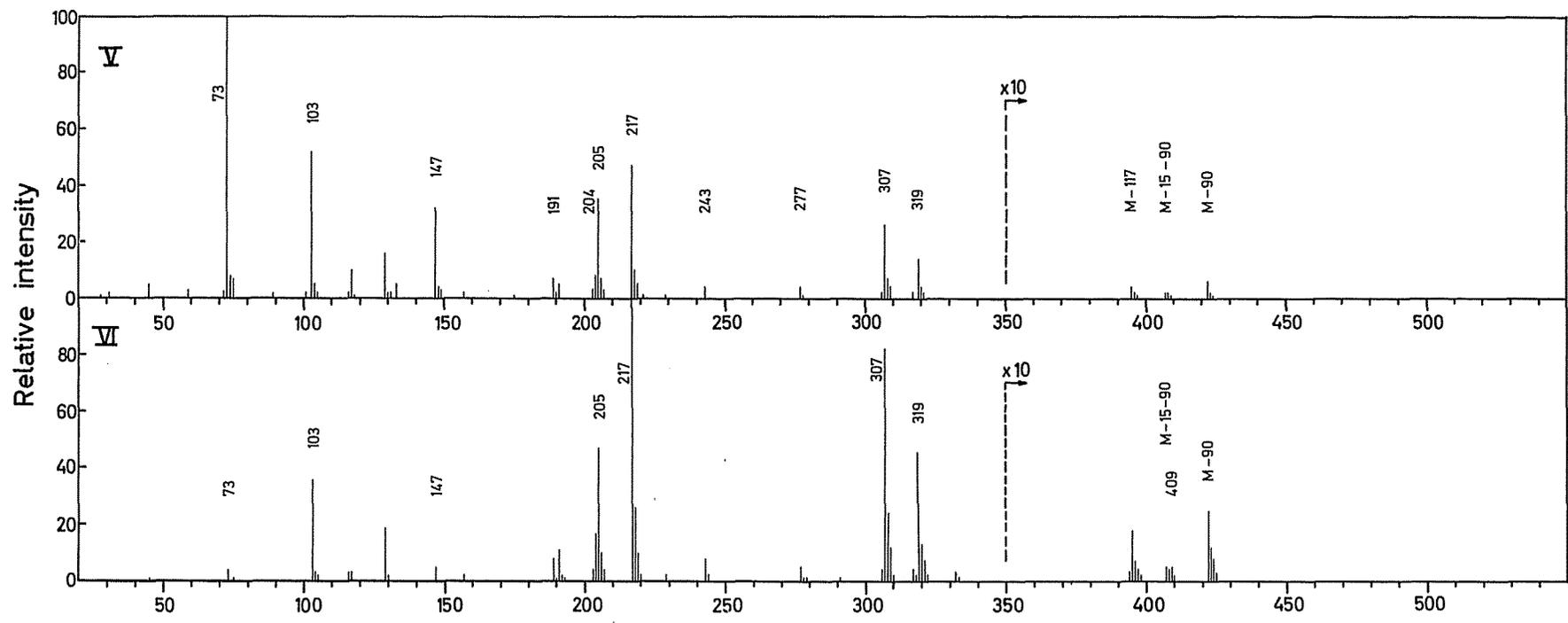


FIG. 2 Mass spectra of the TMS ether of xylitol at 70 eV (V) and 20 eV (VI).

peaks increases somewhat with increasing mass in the low energy spectra compared with the high energy spectra. This advantage for analytical purposes is partly lost by the lower ion yield at low electron energies, however.

Spectra of diastereomeric derivatives. The differences between the spectra for all investigated diastereomeric alditols were found to be very small and restricted to differences in the relative intensities of the peaks. The spectra at 70 eV for arabinitol in Fig. 1 and xylitol in Fig. 2 are illustrative. The magnitude of the intensity differences for hexitols are exemplified by the values in Table 1 for the investigated derivatives. An observation based upon the knowledge of the formation paths for the abundant ions is a comparatively high intensity of the peaks from the cleavage of the C-3 to C-4 bond for galactitol and the C-2 to C-3 and C-4 to C-5 bonds for glucitol and mannitol. Values for glucitol at 20 eV are incorporated in the table for comparison. The differences between the investigated diastereomers are of the same order of magnitude as those for the methyl and acetyl derivatives.^{1, 2, 3}

Structural information from the spectra. The most outstanding features in the mass spectra of the alditol TMS ethers are common and characteristic for all alditols. This permits an easy differentiation of alditol derivatives from derivatives of other carbohydrates. The number of C atoms in the alditol can be easily determined. Peaks at M-15, M-90, M-90-15 and the highest mass of the series 217, 319, and 421 are suitable

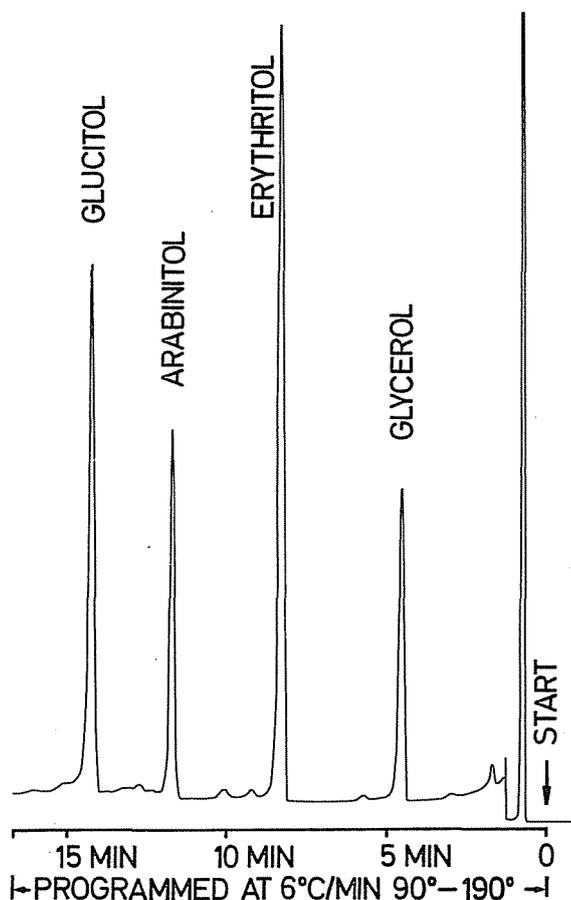


FIG. 3 Separation of alditols as trimethylsilyl ethers. Total ion current trace at 20 eV from LKB 9000. Column: 300 × 0.2 cm ID stainless steel. Column packing: 3% DC QF-1 on Gas Chrom Q 100/120 mesh. Carrier gas: He. Flow rate: 29 ml/min. Sample: 1-3 µg of each TMS ether.

for this purpose. The differentiation of diastereomeric derivatives requires spectra of high quality due to the small differences between these spectra.

Gas Chromatography. The TMS derivatives were found to be well suited for introduction into the mass spectrometer through the gas chromatography inlet. Fig. 3 shows a chromatogram of the derivatives whose mass spectra are given in Fig. 1.

The standard method for gas chromatographic separation of diastereomeric alditols makes use of the acetates. A satisfactory separation of the diastereomeric TMS derivatives is more difficult to achieve on both polar and nonpolar stationary phases.^{cf. 10} In connection with the present investigation the available alditols were studied on four representative stationary phases. The retention times for the diastereomeric TMS derivatives were found to differ by less than 10% on OV-1 (non-polar), DC QF-1 and GE XE-60 (medium-polar), and ECNSS-M (polar).

TABLE I. INTENSITIES FOR SIGNIFICANT PEAKS IN THE SPECTRA OF TMS ETHERS OF DIASTEREOMERIC HEXITOLS GIVEN AS % Σ_{20} *

<i>m/e</i>	73	147	103	205	307	409	217	319	421
Glucitol, 70 eV	21.7	6.4	6.9	10.9	3.5	0.1	5.1	10.7	0.5
Galactitol, 70 eV	20.6	6.1	8.3	8.1	6.7	0.1	9.1	6.1	0.6
Mannitol, 70 eV	21.1	6.0	6.1	11.5	3.0	0.1	5.1	12.0	0.4
Glucitol, 20 eV	0.7	0.7	2.7	12.4	8.9	0.4	6.9	27.5	1.3

* Percentages of the sum of all peaks above *m/e* = 20 greater than 1% of the base peak.

EXPERIMENTAL

Threitol was prepared by reduction of threose. The other alditols were commercial samples. The TMS derivatives were prepared in pyridine according to Sweeley *et al.*¹⁰ and dissolved in anhydrous diethyl ether after evaporation.

The instrument used was a LKB 9000 gas chromatograph-mass spectrometer. The samples were introduced through the QF-1 column described under Fig. 3. The temperature of the molecule separator was 210°C and of the ion source 270°C. The spectra were corrected for column bleeding.

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