Specific features of the interaction of methyl ethers of methyl (methyl-α-D-galactopyranoside)uronate with trimethylsilyl ions in the gas phase

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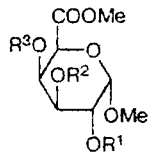
Specific features of the interaction between trimethylsilyl ions and methyl (methyl-α-D-galactopyranoside)uronate and its methyl ethers were revealed. It was shown that a hydrogen atom is generated when the trimethylsilyl ion is located at hydroxyl group. This atom migrates over the methoxy and hydroxyl groups toward the glycoside methoxy group, resulting in the formation of $[Me+SiMe_3-MeOH]^+$ ions.

Key words: chemical ionization, reagent gas, trimethylsilyl ion, methyl ethers of uronates.

It has been shown previously[1,2] that methyl ethers of methyl uronates form protonated molecular ions (PMI) under conditions of chemical ionization (CI, with isobutane or methane as the reagent gas) whose fragmentation mainly involves elimination of a proton of the reagent gas (irrespective of its location) with the substituent at the C(1) atom, which is evidence for the high migration ability of the nonsolvated proton and its tendency to undergo chelation.

In this work, specific features of the interaction of complex polyfunctional molecules with bulky $SiMe_3^+$ ions have been revealed using methyl (methyl-α-D-galactopyranoside)uronate and its methyl ethers (**1—8**) as an example. The $SiMe_3^+$ ions are incapable of either migration from one functional group to another or chelation with neighbouring functional groups under CI conditions.[3]



1: $R^1 = R^2 = R^3 = Me$
2: $R^1 = H$, $R^2 = R^3 = Me$
3: $R^1 = R^3 = Me$, $R^2 = H$
4: $R^1 = R^2 = Me$, $R^3 = H$
5: $R^1 = Me$, $R^2 = R^3 = H$
6: $R^1 = R^3 = H$, $R^2 = Me$
7: $R^1 = R^2 = H$, $R^3 = Me$
8: $R^1 = R^2 = R^3 = H$

Experimental

Mass spectra were recorded on a Kratos-MS-30 mass spectrometer (energy of ionizing electrons of 200 eV) at a temperature of the ion source of 150 °C. The pressure of the reagent gas (0.2 Torr) was kept constant with the use of an external manometer mounted on the inlet system. Tetramethylsilane (Merck) of 99.7% purity was used. The samples were introduced through a heated direct inlet system.

Results and Discussion

The CI mass spectra of methyl uronates **1—8** (with tetramethylsilane as the reagent gas) are listed in Table 1. All studied compounds form fairly stable $[M+SiMe_3]^+$ ions with the trimethylsilyl ion; their further fragmentation depends on the type of substituents R^1, R^2, and R^3. Fragmentation of the $[M+SiMe_3]^+$ ion of compound **1**, which contains no hydroxyl groups, results in ions with *m/z* 105 (Me_3SiHO^+Me), which are usually formed by the interaction of methyl ethers with trimethylsilyl ions.[3,4] The reaction of these ions, which contain a mobile proton, and of ions with *m/z* 91 that are generated in the interaction of Me_3Si^+ with the water that is always present in the ion source with molecules of **1** gives $[M+H]^+$ ions with *m/z* 265. Their fragmentation occurs with the loss of an anomeric methoxy group and a methoxycarbonyl group, and results in ions with *m/z* 233 and 205, respectively.[1,2] Ions with *m/z* 233 can also be

Scheme 1

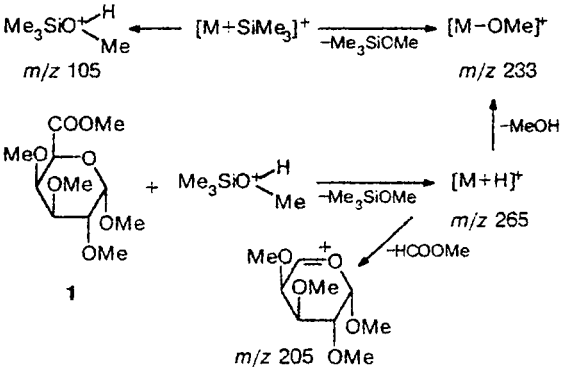


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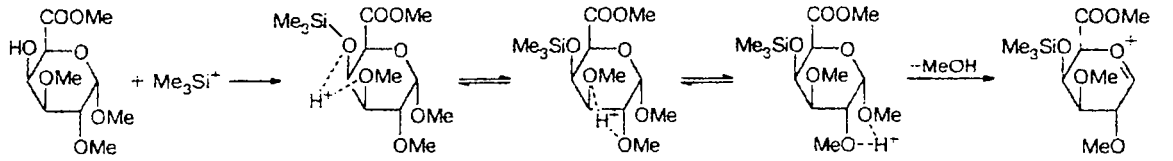
Table 1. CI mass spectra of methyl (methyl-α-D-galactopyranoside)uronate and its methyl ethers (**1—8**) (with tetramethylsilane as the reagent gas)

Ion	*m/z* (*I* (%))							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
$[M+SiMe_3]^+$	337 (100)	323 (40.6)	323 (100)	323 (100)	309 (50.9)	309 (61.7)	309 (61.2)	295 (34.1)
$[M+SiMe_3-MeOH]^+$	305 (—)	291 (19.4)	291 (33.2)	291 (47.6)	277 (43.7)	277 (29.3)	277 (33.5)	263 (52.8)
$[M+H]^+$	265 (36.8)	251 (4.8)	251 (29.6)	251 (10.8)	237 (8.5)	237 (27.1)	237 (14.4)	223 (8.1)
$[M+H-MeOH]^+$	233 (35.7)	219 (37.4)	219 (46.7)	219 (33.6)	205 (51.6)	205 (64.0)	205 (26.2)	191 (23.4)
$[M+H-HCOOMe]^+$	205 (35.7)	191 (22.8)	—	191 (6.5)	—	—	—	—
$Me_3SiCH_2SiMe_2HO^+Me$	177 (36.9)	177 (52.5)	177 (50.1)	177 (37.1)	177 (70.3)	177 (20.6)	177 (72.3)	177 (44.5)
Me_3SiHO^+Me	105 (83.6)	105 (100)	105 (87.8)	105 (84.1)	105 (100)	105 (100)	105 (100)	105 (100)
$Me_3SiO^+H_2$	91 (18.5)	91 (14.5)	—	91 (20.2)	91 (46.9)	91 (5.6)	91 (5.6)	—

Scheme 2



4 **A** $[M+SiMe_3-MeOH]^+$ **B** *m/z* 291

formed from the $[M+SiMe_3]^+$ ion as a result of elimination of the Me_3SiOMe molecules; however, in this case any methoxy group in molecule **1** can be lost because of the inability of the trimethylsilyl group to migrate[5] (Scheme 1).

Fragmentation of the $[M+SiMe_3]^+$ ions of uronates **2—8** containing hydroxyl groups is accompanied by migration of a hydrogen atom from the OH group toward the methoxy group at the C(1) atom to form a $[M+SiMe_3-MeOH]^+$ ion. The $[M+SiMe_3]^+$ ion contains a mobile hydrogen atom (Scheme 2, ion **A**) that migrates to the glycoside center (like the proton of the reagent gas in protonated molecular ions of monosaccharides) and is eliminated together with the glycoside methoxy group, resulting in the formation of a glycosyl ion of structure **B**.

The ability of $[M+SiMe_3]^+$ ions of uronate **4** to generate glycosyl ions **B** suggests that the adjacent functional groups, which contain no mobile hydrogen atoms, can participate in the H^+ migration toward the glycoside center since direct interaction of the proton of the hydroxyl group at the C(4) atom with the methyl group at the C(1) atom of the monosaccharide cycle is impossible because of the mutual *trans*-orientation of both groups. For instance, the transfer of a proton from OH to a OMe group occurs in the interaction of the trimethylsilyl ion with *cis*-4-methoxycyclohexan-1-ol, whereas no such migration occurs in the *trans*-isomer.[6]

The position of the hydroxyl group in the monosaccharide cycle has little effect on the formation of type **B** glycosyl ions (see Table 1). This indicates that the migration of a proton from one functional group to another is a low-energy process.

Using $SiMe_3^+$ ions allows one to generate ions with a proton localized at a certain part of a polyfunctional molecule containing hydroxyl groups and to estimate the capability of the proton to migrate toward the reaction center. The availability of two or three hydroxyl groups in the pyranose cycle of monosaccharide (compounds **5—8**) results in a decrease in the stability of $[M+SiMe_3]^+$ adducts due to the increase in the possibility of eliminating a methanol molecule from the latter.

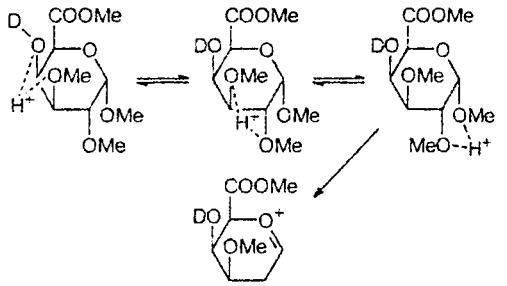
A study of the mass spectra of uronates **1—8** under CI conditions using CD_4 as the reagent gas showed (Table 2) that not only the deuterons of the reagent gas but also the protons of the hydroxyl groups of monosaccharide participate in elimination of a methanol mol-

Table 2. CI mass spectra of uronates **1—4** (with CD_4 as the reagent gas)

Ion	*m/z* (*I* (%))			
	1	**2**	**3**	**4**
$[M+D]^+$	266 (2.0)	252 (7.5)	252 (4.6)	252 (5.8)
$[M+H-CH_3OH]^+$	232 (14.0*)	220 (100)	220 (100)	220 (100)
$[M+D-CH_3OD]^+$	233 (100)	219 (47.0)	219 (64.0)	219 (63.5)

* This value corresponds to the intensity of the isotope current.

Scheme 3



ecule from the $[M÷D]^+$ ions with the formation of glycosyl ions; the position of the hydroxyl group in the monosaccharide cycle has little effect on the possibility of the migration of the proton toward the reaction center. Thus, for uronates in which the hydroxyl group and the substituent at the C(1) atom are either in *cis*- or in *trans*-positions, no differences in the ability of the proton to migrate are observed. This is due (as in the case considered above) to the presence of functional groups between the substituents at the C(1) and C(4) atoms; these groups favor transfer of the proton over the cycle (Scheme 3), which results in an equilibrium of various protonated forms and, in the case of the elimination of functional groups, in the formation of the most stable product, a glycosyl cation.

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