

MASS SPECTRA OF METHYL 4,6-O-BENZYLIDENEGLYCOSIDES

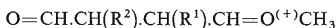
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The mass spectra of methyl 4,6-O-benzylidene- α -D-glucopyranoside (*I*), the 2-deoxy (*II*), 3-deoxy (*III*), 2,3-dideoxy (*IV*), and 2,3-dideoxy-2-ene (*V*) derivatives and methyl ethers *VI*–*VIII* were measured. Marked differences in spectra and replacement of the hydrogen atoms in the hydroxylic functions by deuterium made possible to discuss formation of structurally significant ionic species. It is shown that position of the hydroxylic function on the pyranoside ring as well as the methylation of hydroxylic functions alters routes of decomposition of the molecular ion.

The mass spectra of methyl 4,6-O-benzylidene- α -D-glucopyranoside (*I*), its deoxy derivatives *II*–*V* (Fig. 1), and the methyl ethers *VI*–*VIII* differ from each other. The spectra become simple with the decreasing number of hydroxylic functions. The "h rupture" reported by Chizov and coworkers^{1–3} asserts itself with all compounds *I*–*VIII* and affords ions of the *a* and *h* type. With deuterated analogues of compounds *I*–*III*, *VI* and *VII*, the ions of the type *a* retain deuterium in ratios depending on the degree of deuteration. This finding is in accordance with the structure



The rupture into two halves predominates with compounds *IV* and *V* over other fragmentations and is thus preferred in the case of a decreased possibility of competitive ruptures caused by substituents. The ratio of relative abundances of *a*-ions and *h* ions is 100 : 3 with compound *IV* and 83 : 100 with compound *V*. The considerably higher relative abundance of *h* ions with compound *V* may be explained, e.g., by the stability of the simultaneously formed radical¹. $\text{OCH}.\text{CH}=\text{CH}.\dot{\text{C}}\text{H}.\text{OCH}_3$ which is caused by conjugation with the double bond. The ions of the type *a* with compound *II* and to a lesser extent, with compound *I* split off a molecule of water by the 2,3-elimination under the formation of *b*-ions. The *b*-ions in the spectrum of the compound *II-d*₁ do not contain any deuterium; one deuterium atom is retained in the case of compound *I-d*₂.

* The modified version received January 28th, 1972.

The occurrence of the ions m/e 179 (c) appears characteristic of the molecular arrangement in benzylideneglycosides. We did not find any metastable transition for the formation or decomposition of these ions in spectra of the investigated compounds. The *c*-ions are present in spectra of all compounds carrying a free hydroxylic function at the $C_{(3)}$ carbon atom. In spectra of the deuterio analogues *II* and *VI* the ions m/e 179 are shifted by one mass unit; in the case of compound *I* these ions are shifted by one and two mass units. When the hydroxyl group at the $C_{(2)}$ carbon atom is replaced by a methoxyl group, the ions m/e 179 are accompanied by the ions m/e 193; both ions of the deuterio analogues contain deuterium. As shown by the peak matching technique in the case of compound *I*, the ions m/e 179 possess the elemental composition $C_{10}H_{11}O_3$. However, on the basis of the present evidence it is not possible

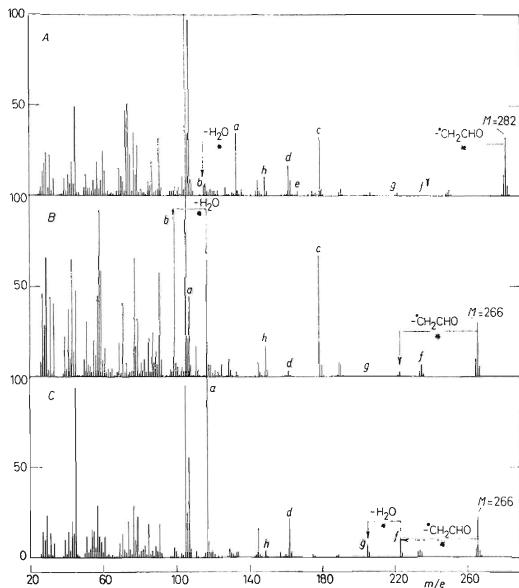
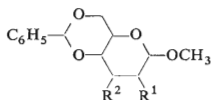


FIG. 1

A Methyl 4,6-O-Benzylidene- α -D-glucopyranoside (*I*); B Methyl 4,6-O-Benzylidene-2-deoxy- α -D-arabino-hexopyranoside (*II*); C Methyl 4,6-O-Benzylidene-3-deoxy- α -D-ribo-hexopyranoside (*III*)



- I*, R¹ = R² = OH
II, R¹ = H, R² = OH
III, R¹ = OH, R² = H
IV, R¹ = R² = H

- V*, R¹ = R² = O (Pyranosenide)
VI, R¹ = OCH₃, R² = OH
VII, R¹ = OH, R² = OCH₃
VIII, R¹ = R² = OCH₃

to propose any scheme of their formation or the detailed structure of these ions. As similar ions have not been so far studied, no analogies can be used. The ions m/e 179 are without any doubt of two types. Both these types probably contain the C₍₃₎ carbon atom along with the appropriate hydrogen atom and hydroxyl, the C₍₄₎ carbon atom, the vicinal oxygen atom and the benzylidene residue. The first type c^1 contains in addition the C₍₆₎ carbon atom along with the appropriate oxygen atom while the c^2 ion contains an additional C₍₂₎ carbon atom with its substituent. We can not exhaustively explain the exclusive role of the hydroxyl at the C₍₃₎ carbon atom as the necessary condition for the formation of c -ions in contrast to other substituents at C₍₃₎, *e.g.*, —OCH₃, —Cl, —S—C₆H₄—CH₃ (ref.⁴). The striking difference in behaviour of compounds bearing hydroxyl and methoxyl groups can not be explained by different electron and spatial properties of these substituents. A similar marked difference in behaviour of the hydroxyl and methoxyl has been observed in homogeneous phase with the reaction in which the oxonium ion asserts itself as intermediate and where the hydrogen transfer represents the necessary step. To our opinion, the hydrogen transfer from the hydroxyl at the C₍₃₎ carbon atom is necessary for the formation of both c^1 ions and c^2 ions.

The e -ions represent further ionic species. Their m/e value is 167 with compounds carrying a hydroxylic function at the C₍₃₎ carbon atom (with *I-d*₂ and *VI-d*₁, a shift to m/e 168 is observed). When the hydroxylic function is replaced by the methoxyl group (*VII* and *VIII*) or chlor atom⁴, the m/e value is 181 or 185, resp. (with *VII-d*₁, deuterium is not retained). The e ions are probably formed analogously to c^1 -ions but the hydrogen transfer from the hydroxylic function does not represent the necessary interstage.

The d ions (m/e 162) are abundant in spectra of compounds *I* and *III*, poorly intensive with compounds *II*, *VI* and *VII* and absent with compounds *IV*, *V*, and *VIII*. In spectrum of compound *VI*, the ions m/e 176 are present in addition to the ions m/e 162. The ions m/e 162 with compounds *III-d*₁ and *VII-d*₁ and the ions m/e 176 with compound *VI* do not retain deuterium; with compounds *I-d*₂ and *VI-d*₁, the d ions (m/e 162) contain one deuterium atom only by 20%. With compound *IIIa* in which one hydrogen atom at position C₍₃₎ is replaced by deuterium, the ions m/e 162 are not shifted to m/e 163 and do not therefore contain in their structure the C₍₃₎ carbon

atom. The elemental composition of *d* ions originated from *I* is $C_{10}H_{10}O_2$ as determined by high resolution measurement. The ions m/e 162 and 176 with *VI* and the partial shift of ions m/e 162 to 163 with *I-d*₂ give evidence that at least two types of *d* ions with compounds *I* and *VI* are formed. In the case of compound *III*, an increase of the relative abundance of *d* ions (m/e 162) may be observed in contrast to compound *I* and especially compounds *II*, *VI* and *VII* (Fig. 1). Methyl ethers of methyl 3-deoxy-D-glycopyranosides are characteristic by cleavage under the formation of ions containing the $C_{(4)}$ and $C_{(3)}$ carbon atoms³ (type K^1). The *d* ions with compound *III* and a major part of *d* ions with compounds *I*, *II*, *VI* and *VII* may be analogous to ions of the type K^1 and may therefore possess the structure of the 2-phenyl-1,3-dioxane ring. The ions m/e 162 of this structure are also characteristic of 1,3,6,8-tetraoxabicyclo[4.4.0]decanes². The second type of *d* ions which occur to a far lesser extent, namely, the ions retaining deuterium (with compound *I*) or the methyl group (m/e 176), probably contain the $C_{(2)}$, $C_{(3)}$, and $C_{(4)}$ carbon atoms and the benzylidene part of molecule without any change of the elemental composition $C_{10}H_{10}O_2$. There is no evidence in spectra for their formation.

In all spectra of the present compounds, we have also observed the structurally non-characteristic ion $(M-1)^+$ and $(M-31)^+$ which are formed³ by the α -cleavage in respect to the glycosidic oxygen atom. The poorly intensive *f* ions $(M-43)^+$ with compounds *I-IV* are formed by removal of the radical $\dot{C}H_2-CH=O$. The *f* ions retain completely deuterium, i.e., this radical contains most probably the carbon atoms $C_{(6)}$ and $C_{(5)}$, and the ring oxygen atom⁶. Furthermore, the *f* ions (m/e 223) with compound *III* split off a molecule of water under the formation of the *g*-ion (m/e 205). With compound *IIIa* in which one hydrogen atom at $C_{(3)}$ is replaced by deuterium, the *g* ions are shifted by 90% to m/e 206. The hydrogen atom at the $C_{(3)}$ carbon is thus almost exclusively not involved in the removal of the molecule of water ($f \rightarrow g$).

The mass spectra of methyl ethers of methyl 4,6-O-benzylidene-glycosides are as expected considerably simple. In contrast to *a*, *h*, *b*, *c* and *d* ions, the ions typical of methyl ethers of glycopyranosides^{3,6-9} predominate, namely the ions m/e 74 (with compounds *VI* and *VII*), m/e 88 (*VIII*), m/e 75 (*VII* and *VIII*), m/e 87 (*VI* and *VII*), and m/e 101 (*VIII*). Analogously to dideoxy compounds *IV* and *V*, the ions m/e 107 are absent in spectrum of the permethylated benzylidene-glycoside *VIII*.

In spectra of deuterated analogues *I-d*₂, *II-d*₁, *III-d*₁, *VI-d*₁, and *VII-d*₁, the ions m/e 107 shift to m/e 108; they contain therefore the hydrogen atom of the hydroxylic function and possess the structure of a protonated benzaldehyde². The spectra of all the studied compounds contain ions of the aromatic type, m/e 77 ($C_6H_5^+$), 79 ($C_6H_7^+$), 91 ($C_7H_7^+$), 105 ($C_6H_5CO^+$).

EXPERIMENTAL

Melting points were taken on a heated microscope stage (Kofler block). Optical rotations were measured in chloroform unless stated otherwise.

Materials. Methyl 4,6-O-benzylidene- α -D-glucopyranoside¹⁰ (*I*), m.p. 166–167°C, $[\alpha]_D^{22} +92.1^\circ$ (c 1.02; methanol); methyl 4,6-O-benzylidene-2-deoxy- α -D-arabino-hexopyranoside^{11,12} (*II*), m.p. 151–152°C, $[\alpha]_D^{20} +90^\circ$ (c 1.0; acetone); methyl 4,6-O-benzylidene-3-deoxy- α -D-ribo-

hexopyranoside¹³ (*III*), m.p. 190–191°C, $[\alpha]_D^{20} +124.1^\circ$; methyl 4,6-O-benzylidene-2,3-dideoxy- α -D-*erythro*-hexopyranoside¹¹ (*IV*), m.p. 83–84°C, $[\alpha]_D^{20} +124.8^\circ$; methyl 4,6-O-benzylidene-2,3-dideoxy- α -D-*erythro*-hex-2-enopyranoside¹¹ (*V*), m.p. 117.5–119°C, $[\alpha]_D^{23} +129.2^\circ$; methyl 4,6-O-benzylidene-2-O-methyl- α -D-altropyranoside¹⁴ (*VI*), m.p. 97–99°C, $[\alpha]_D^{20} +102.1^\circ$; methyl 4,6-O-benzylidene-3-O-methyl- α -D-altropyranoside¹⁴ (*VII*), m.p. 131–133°C, $[\alpha]_D^{20} +103.2^\circ$; methyl 4,6-O-benzylidene-2,3-di-O-methyl- α -D-altropyranoside¹⁵ (*VIII*), m.p. 83–84°C, $[\alpha]_D^{20} +92.4^\circ$.

Methods. The deuterated glycosides *I–III* were prepared by adding a twentyfold molar excess of D₂O to a solution of the appropriate compound in pyridine. The resulting reaction mixture was kept for 3 hours over concentrated sulfuric acid under diminished pressure (10⁻¹ Torr). The dried crystals were directly introduced into the mass spectrometer. The deuterium content was determined from mass spectra at the ionizing potential of 11 e.v. Compound *I*: *d*₁ 17%, *d*₂ 83%; *II*: *d*₀ 24%, *d*₁ 76%; *III*: *d*₀ 20%, *d*₁ 80%. Methyl 4,6-O-benzylidene-3-deoxy-3-deuterio- α -D-*arabino*-hexopyranoside (*IIIa*) was prepared by the lithium aluminum deuteride reduction of methyl 4,6-O-benzylidene-2,3-anhydro- α -D-mannopyranoside in tetrahydrofuran¹⁶, purified by chromatography on silica gel, and crystallised from a mixture of benzene and light petroleum, m.p. 109–110°C. The mass spectra were recorded on a Gas Chromatograph – Mass Spectrometer LKB 9000, low resolution, ionizing energy 70 e.v., temperature of the ion source 230°C, direct introduction of samples at 20–50°C.

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