Mass Spectrometry of Some Unsaturated Monosaccharides and Their Peracetyl Derivatives

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Received August 28, 1969

The fragmentation of D-arabinal, D-xylal, D-galactal, D-glucal, ethyl-2,3-dideoxy-α,D-*erythro*-hex-2-enopyranoside, their *O*-deuterated analogues and peracetyl derivatives was studied. The fragmentation of free and peracetylated 1,2-unsaturated monosaccharides differs significantly from that of ethyl-2,3-dideoxy-α,D-*erythro*-hex-2-enopyranoside and its peracetyl derivative. Characteristic differences were found when comparing quantitatively the spectra of stereoisomers of 1,2-unsaturated monosaccharides with hydroxy or acetyl groups in *cis* and *trans* position at carbon atoms C_3 and C_4. Fragmentation mechanisms of the studied compounds are suggested and discussed in this paper.

Some peracetyl derivatives of 1,2- and 2,3-unsaturated hexopyranosides [1] and also D-glucal [2] were investigated by mass spectrometry. This paper deals with the fragmentation of 1,2-unsaturated pentopyranoses and some unsaturated hexopyranoses and their peracetyl derivatives, as well. Recorded and interpreted were spectra of substances as listed in Table 1 and also spectra of *O*-deuterated compounds *V*—*VIII* and *X* (*Va*, *VIa*, *VIIa*, *VIIIa*, *Xa*).

Table 1

Nr.	Compound	M.p.	$[\alpha]_D^{24}$	*c*; Solvent	Ref.
I	3,4-di-*O*-acetyl-D-arabinal	—	+263.5	1.5; $CHCl_3$	[3]
II	3,4-di-*O*-acetyl-D-xylal	—	−315.0	1.2; $CHCl_3$	[4] Vol. 1, p. 184
III	3,4,6-tri-*O*-acetyl-D-galactal	28—30	− 12.1	1.3; $CHCl_3$	[4] Vol. 2, p. 457
IV	3,4,6-tri-*O*-acetyl-D-glucal	54—55	− 15.4	1.5; C_2H_5OH	[4] Vol. 2, p. 406
V	D-arabinal	80—82	+197.4	2.0; H_2O	[3]
VI	D-xylal	—	−245.4	2.0; H_2O	[4] Vol. 2, p. 184
VII	D-galactal	98—100	− 6.6	2.0; H_2O	[4] Vol. 2, p. 457
VIII	D-glucal	57—60	− 8.0	2.0; H_2O	[4] Vol. 2, p. 406
IX	ethyl-4,6-di-*O*-acetyl-2,3-dideoxy-α,D-*erythro*-hex-2-enopyranoside	80—82	+103.0	1.5; C_6H_6	[5]
X	ethyl-2,3-dideoxy-α,D-*erythro*-hex-2-enopyranoside	101	+100.1	1.5; C_2H_5OH	[5]

Experimental

Compounds for measuring mass spectra were prepared according to literature given in Table 1. Mass spectra were taken with a MCh 1306 apparatus (U.S.S.R.) adapted for a direct introduction of samples into the ionization chamber at the ionizing electron energy 70 eV. Temperature in the vaporization locus 20—30°C, temperature in the ionization chamber 100°C.

Deuterization of compounds *V*, *VI*, *VII*, *VIII*, *X* was carried out directly in the mass spectrometer by evaporation of D_2O from the solutions of samples. The achieved degree of deuterization of substances *Va*, *VIa*, *VIIa*, *VIIIa*, *Xa* was found to be 94, 92, 89, 91, 85%, respectively.

Results and Discussion

Fragmentation of both 3,4-di-*O*-acetyl-D-arabinal (*I*) and 3,4-di-*O*-acetyl-D-xylal (*II*) shows qualitatively the same pattern and is exemplified with substance *I* (Fig. 1) in Scheme 1. The decomposition of the molecular ions follows three pathways. The loss of the radical •OAc from carbon atom C_3 initiates series *A*; the next step is the expulsion of the molecule of acetic acid. Series *B* is triggered by the stepwise elimination of acetic acid, ketene and hydrogen atom. The decomposition of the pyranoid ring affords ions of series *C* at *m/e* 157 (this mechanism is discussed later) which, after the loss of two molecules of ketene led to ions at *m/e* 115 and 73.

Mass spectra of 3,4,6-tri-*O*-acetyl-D-galactal (*III*) and 3,4,6-tri-*O*-acetyl-D-glucal (*IV*) are qualitatively consistent with that of compound *IV* as reported earlier [1] excepting that little abundant ions $(M - \bullet OAc)^+$ at *m/e* 213 and $(M - \bullet OAc - AcOH)^+$ at *m/e* 153 belonging to series *A* were found in our spectra.

When comparing mass spectra of pairs of stereoisomers *I* + *II* and *III* + *IV* it becomes evident that peaks of ions of series *A* and *B* (and also series beginning with the loss of radical $\bullet CH_2OAc$ from hexopyranosides) are of the same intensity. On the other hand, peaks of ions of series *C* (Table 2) are approximately twice to three times higher in compounds *I* + *III* (*cis* position of acetyl groups at O_3 and C_4) than in

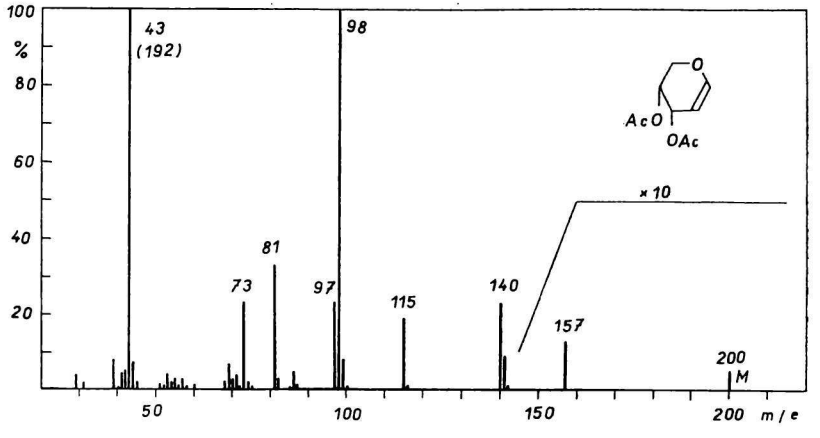
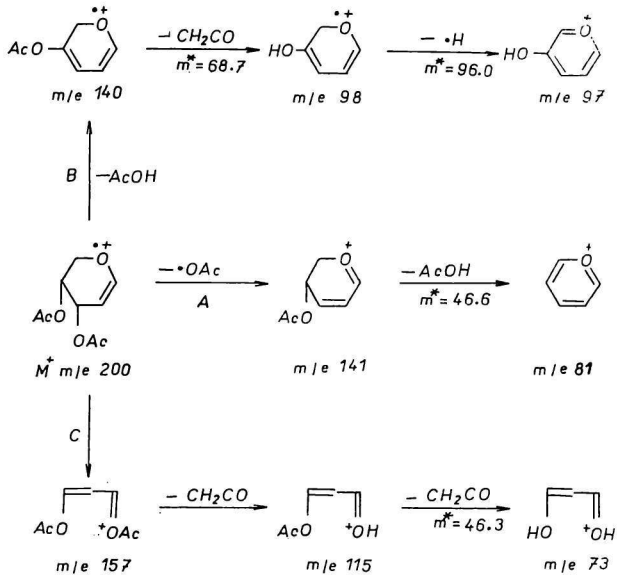


Fig. 1. Mass spectrum of 3,4-di-*O*-acetyl-D-arabinal (*I*).



Scheme 1

those of *II* + *IV* (*trans* position of acetyl groups at C_3 and C_4). It is possible to make use of this phenomenon to distinguish stereoisomers of peracetyl derivatives of 1,2-unsaturated pyranosides.

Table 2

Compound	Position of OAc at C_3 and C_4	Relative intensities of peaks at		
		m/e 157	*m/e* 115	*m/e* 73
I	*cis*	1.1	19.5	23.4
II	*trans*	0.4	8.1	11.8
III	*cis*	0.9	17.6	15.9
IV	*trans*	0.3	7.8	7.1

Whereas the decomposition of peracetylated 1,2-unsaturated pentopyranoses *I* and *II* preponderantly follows series *B*, that of D-arabinal (*V*) (Fig. 2) and D-xylal (*VI*) proceeds almost exclusively according to series *C*. Thus ions at *m/e* 73 (75 in the spectra of *O*-deuterated compounds *Va*, *VIa*) ($m^* = 46.0$; $116 \rightarrow 73$) are formed from molecular ions. A faint fragmentation of series *A* and *B* is seen in the little pronounced peaks of ions $(M - \cdot OH)^+$ at *m/e* 99 (100), $(M - \cdot OH - H_2O)^+$ at *m/e* 81 (81) and $(M - H_2O)^+$ at *m/e* 98 (99).

D-Galactal (*VII*) and D-glucal (*VIII*) (Fig. 3) reveal, likewise substances *V* and *VI*, a dominant formation of ions at *m/e* 73 (75) ($m^* = 36.5$; $146 \rightarrow 73$). Of other

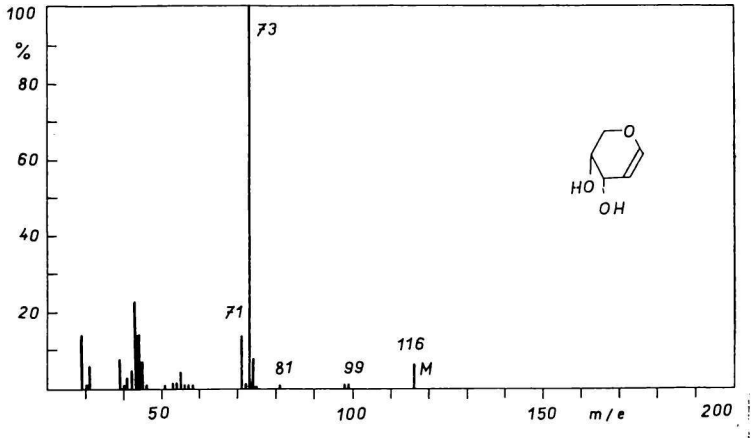


Fig. 2. Mass spectrum of D-arabinal (*V*).

series, there are little abundant peaks of ions $(M - \cdot OH)^+$ at *m/e* 129 (131), $(M - H_2O)^+$ at *m/e* 128 (130), $(M - \cdot CH_2OH)^+$ at *m/e* 115 (117) and $(M - \cdot CH_2OH - H_2O)^+$ at *m/e* 97 (98) in their spectra.

A higher stability of isomers possessing the *trans* configuration of hydroxyl groups at carbons C_3 and C_4 has been observed when comparing the relative intensity of molecular ions. Thus the relative intensity of pairs of isomers was found to be 6.6%

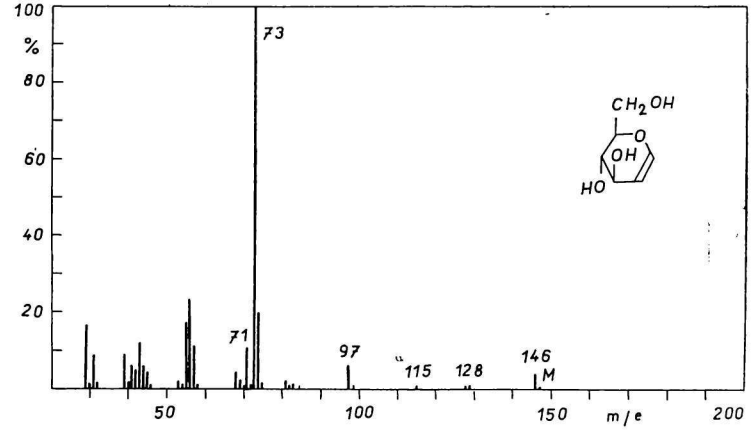


Fig. 3. Mass spectrum of D-glucal (*VIII*).

and 11.5% with D-arabinal and D-xylal and 2.1% and 4.0% with D-galactal and D-glucal. When omitting the slight fragmentation according to series *A* and *B* (and also the loss of $\cdot CH_2OH$ radicals from hexopyranoses) one can see that ions at *m/e* 73 (75) are generated twice as easy in *cis* C_3, C_4 hydroxy isomers. This finding is in accordance with observations made with peracetylated derivatives of *I*—*IV* (Table 2).

Mechanism of fragmentation of series C

Arguments concerning structure and formation of *C* series ions at *m/e* 73 from 1,2-unsaturated pyranoses and those at *m/e* 157, 115 and 73 of their peracetylated derivatives can be summarized as follows:

a) From the same *m/e* values of 1,2-unsaturated hexopyranoses and 1,2-unsaturated pentopyranoses it is deduced that ions under discussion do not contain substituent at C_5.

b) Deuterization analysis of 1,2-unsaturated pyranoses and ions at *m/e* 157, 115 and 73 in the spectra of their peracetylated derivatives evidences the presence of hydroxy or acetoxy group from carbon atoms C_3 and C_4 in the ions under discussion.

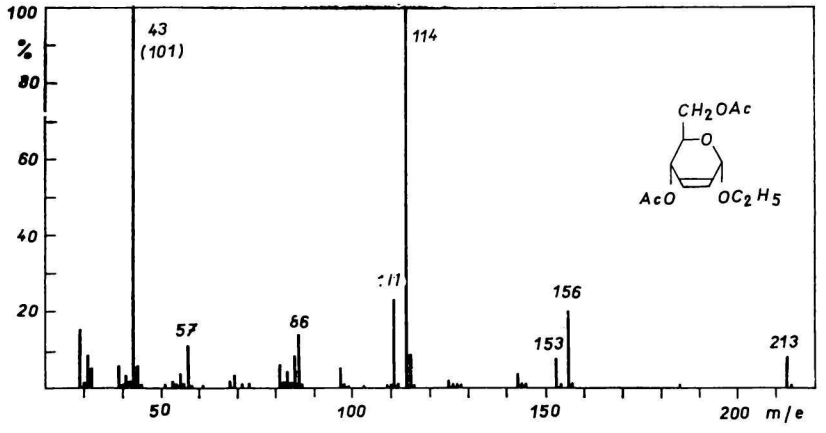


Fig. 4. Mass spectrum of ethyl-4,6-di-*O*-acetyl-2,3-dideoxy--α,D-*erythro*-hex-2-enopyranoside (*IX*).

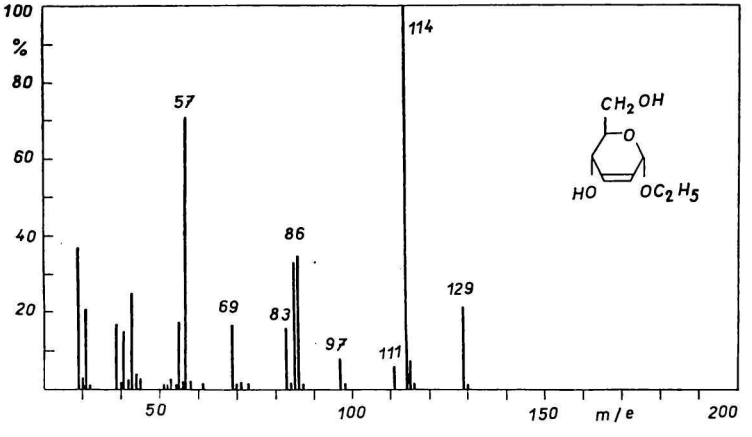


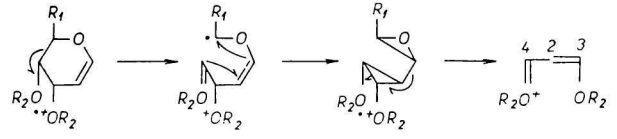
Fig. 5. Mass spectrum of ethyl-2,3-dideoxy-α,D-*erythro*-hex-2-enopyranoside (*X*).

c) The presence of metastables for transition M → 73 in the spectra of compounds *V—VIII* proves their one-step formation from the molecular ions.

d) The fragmentation of 1,2-unsaturated pyranoses and their peracetylated derivatives was found to proceed more intensively with *cis*-oriented hydroxy or acetoxy groups at carbons C_3 and C_4.

e) Ions of series *C* are not formed from 2,3-unsaturated pyranosides upon electron impact (Figs. 4 and 5).

The above-mentioned facts make it possible to formulate the generation of ions of series *C* in Scheme 2. A bicyclic intermediate is formed by the fission of $C_4—C_5$ bond and rearrangement of the double bond from the position 1,2 to carbons C_4 and C_5. This intermediate undergoes further cleavage between C_1 and C_2:



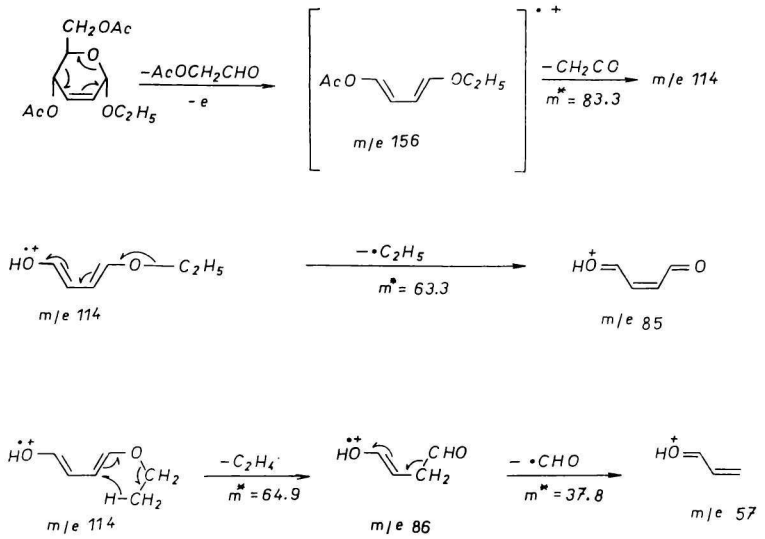
	R_1	R_2	M *m/e*		*m/e*
I, II	H	Ac	200		
III, IV	CH_2OAc	Ac	272	*I—IV*	157
V, VI	H	H	116		
VII, VIII	CH_2OH	H	146	*V—VIII*	73
Va, VIa	H	D	118		
VIIa, VIIIa	CH_2OD	D	149	*Va—VIIIa*	75

Scheme 2

It is assumed that ions at *m/e* 73 (75) are able to split off a molecule of hydrogen to give rise to ions at *m/e* 71 (72) visible in all spectra:

$$\underset{m/e\ 73\ (75)}{HO{=}CH{-}CH{=}CH{-}OH^{+}} \xrightarrow{-H_2} \underset{m/e\ 71\ (72)}{O{\equiv}C{-}CH{=}CH{-}OH^{+}}$$

The mass spectrum of ethyl-4,6-di-*O*-acetyl-2,3-dideoxy-α,D-*erythro*-hex-2-enopyranoside (*IX*) was found to be different in some details from that of methyl-4,6-di-*O*-acetyl-2,3-dideoxy-β,D-*erythro*-hex-2-enopyranoside, published earlier [1]. The compound (*IX*) displays neither peaks of ions $(M - \cdot H)^+$, $(M - \cdot H - AcOH)^+$ and $(M - \cdot H - AcOH - CH_2CO)^+$, nor those of furanoid structure. Peaks $(M - \cdot CH_2OAc)^+$ at *m/e* 185 and $(M - \cdot CH_2OAc - CH_2CO)^+$ at *m/e* 143 are very low in intensity. The main decomposition pathway is retro Diels—Alder fragmentation and the series starting with the loss of a glycosidic $\cdot OC_2H_5$ radical. Retro Diels—Alder fragmentation of molecular ions (Scheme 3) leads to an ion at *m/e* 156 which, after elimination of molecule of ketene, affords ion at *m/e* 114. The disintegration of ions at *m/e* 114 proceeds in two different ways. Ions at *m/e* 85 are formed the $\cdot C_2H_5$ radical being split off. McLafferty rearrangement and elimination of ethylene furnishes ions at *m/e* 86, from which, after the loss of radical •CHO, ions at *m/e* 57 were generated.



Scheme 3

The expulsion of $\cdot OC_2H_5$ radical from the molecular ions gives rise to an ion at *m/e* 213 which loses acetic acid ($m^* = 110.0$; 213 → 153), ketene ($m^* = 80.5$; 153 → → 111) and possibly CH_2O to afford pyronium ions at *m/e* 81.

The mass spectrum of ethyl-2,3-dideoxy-α,D-*erythro*-hex-2-enopyranoside (Fig. 5), as well as that of its *O*-deuterio analogue evidences the cleavage of 2,3-unsaturated pyranosides following two principal fragmentation series. Ions at *m/e* 114 are formed from molecular ions by retro Diels—Alder fragmentation. The shift of *m/e* values of ions at *m/e* 114, 86, 85 and 57 by one mass unit in the spectrum of *O*-deuterio compound *Xa* to values at *m/e* 115, 87, 86 and 58 and also the presence of metastable peaks proves the decomposition of ions at *m/e* 114 as given in Scheme 3. The radicals $\cdot OC_2H_5$ having been split off of the molecular ions, ions $(M - \cdot OC_2H_5)^+$ at *m/e* 129 (131) ($m^* = 95.8$; 174 → 129) are formed. These in turn eliminate H_2O, or CH_3OH molecule to afford ions $(M - \cdot OC_2H_5 - H_2O)^+$ at *m/e* 111 (112), or $(M - \cdot OC_2H_5 - - CH_3OH)^+$ at *m/e* 97 (98). It is not excluded that these fragments lose CO to give rise to ions at *m/e* 83 (84) and 69 (70).

The authors wish to express their thanks to Mr. S. Markovič for his technical assistance.

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Translated by Z. Votický