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MASS SPECTROMETRY OF SULFUR-CONTAINING DERIVATIVES OF SUGARS

PART II. FRAGMENTATION OF SOME 4-THIO-α-D-XYLOSE DERIVATIVES*

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ABSTRACT

The mass spectra of some acetyl, benzoyl, benzyl, isopropylidene, and methyl derivatives of 4-thio-α-D-xylo-pyranose and -furanose have been examined. The molecular peaks are present in the spectra of all of the compounds, except those of the thioacetates and thiobenzoates. The molecular ions of 4-thio-α-D-xylofuranoses are exceptionally stable. The differences in fragmentation of the derivatives of 4-thio-α-D-xylofuranose, as compared to that of the corresponding derivatives of D-xylose, are discussed, and some new fragmentation mechanisms are proposed.

INTRODUCTION

The fragmentation of some methanesulfonic and *p*-toluenesulfonic esters of methyl pentopyranosides has been described[1]. We now describe the fragmentation of some derivatives of 4-thio-α-D-xylose, namely, those substituted with acetyl (Ac), benzoyl (Bz), benzyl ($PhCH_2$), chloro (Cl), isopropylidene (Ip), and methyl (Me) groups.

RESULTS AND DISCUSSION

The spectrum of methyl 2,3-di-*O*-acetyl-4-*S*-acetyl-4-thio-α-D-xylopyranoside (**1**) (see Table I) exhibits all of the features characteristic of the fragmentation of methyl 2,3,4-tri-*O*-acetylpentopyranosides[2]. For comparison, the respective *m/e* values of oxygen analogs[2] are given in fragmentation mechanisms in parentheses. The peaks corresponding to the sulfur-containing ions are shifted upwards by 16 units from the corresponding oxygen derivative, as may be seen in Scheme 1.

The ions at *m/e* 85, 84, 69, and 68 (at *m/e* 69 and 68 in the spectrum of the acetates of methyl pentopyranosides) are probably formed in series B from the ions

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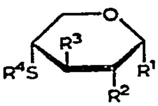
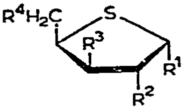
$(\mathrm{M-AcOH-HCOOMe-CH_2CO})^+$ at *m/e* 144 (128) after elimination of AcO· or AcOH, or AcS· or AcSH.



	R¹	R²	R³	R⁴
1	OMe	OAc	OAc	Ac
2	OMe	OBz	OBz	Bz
3	O–Ip–O		OH	$\mathrm{PhCH_2}$
4	O–Ip–O		OD	$\mathrm{PhCH_2^*}$
5	OH	OH	OH	$\mathrm{PhCH_2}$
6	OD	OD	OD	$\mathrm{PhCH_2^*}$
7	OMe	OH	OH	$\mathrm{PhCH_2}$
8	OMe	OD	OD	$\mathrm{PhCH_2^*}$
9	OH	OH	Cl	$\mathrm{PhCH_2}$
10	OD	OD	Cl	$\mathrm{PhCH_2^*}$



	R¹	R²	R³	R⁴
11	O–Ip–O		O–Ip–O**	
12	O–Ip–O		OH	OH**
13	O–Ip–O		OD	OD**

(A) $\mathrm{M}\xrightarrow[-e]{-\cdot\mathrm{OMe}} m/e\ 275\ (259) \xrightarrow{-\mathrm{AcOH}} m/e\ 215\ (199) \xrightarrow{-\mathrm{AcSH}} m/e\ 139\ (139)$

$\xrightarrow{-\mathrm{CH_2CO}} m/e\ 97\ (97)$

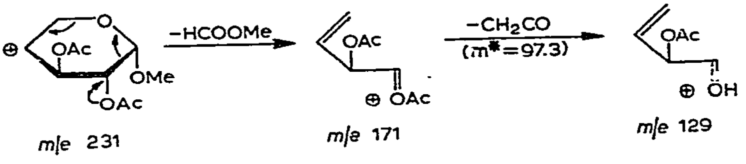
(B) $\mathrm{M}\xrightarrow[-e]{-\mathrm{AcOH}} m/e\ 246\ (230) \xrightarrow[(m^*=140.6)]{-\mathrm{HCOOMe}} m/e\ 186\ (170) \xrightarrow[(m^*=111.6)]{-\mathrm{CH_2CO}} m/e\ 144\ (128)$

$\xrightarrow{-\mathrm{CH_2CO}} m/e\ 102\ (86)$

(C) $\mathrm{M} \longrightarrow m/e\ 173\ (157) \xrightarrow{-\mathrm{CH_2CO}} m/e\ 131\ (115)$

SCHEME 1

In contrast to its oxygen analog, the fragmentation of the molecular ion of **1** was found to proceed through an additional pathway. The AcS· radical is cleaved from C-4, giving rise to ions at *m/e* 231, from which HCOOMe and $\mathrm{CH_2CO}$ (see Scheme 2) are obtained.



SCHEME 2

The fragmentation of the molecular ion of methyl 2,3-di-*O*-benzoyl-4-*S*-benzoyl-4-thio-α-D-xylopyranoside (**2**) (see Table I) is initiated by the splitting of

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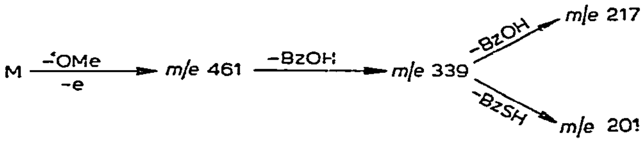
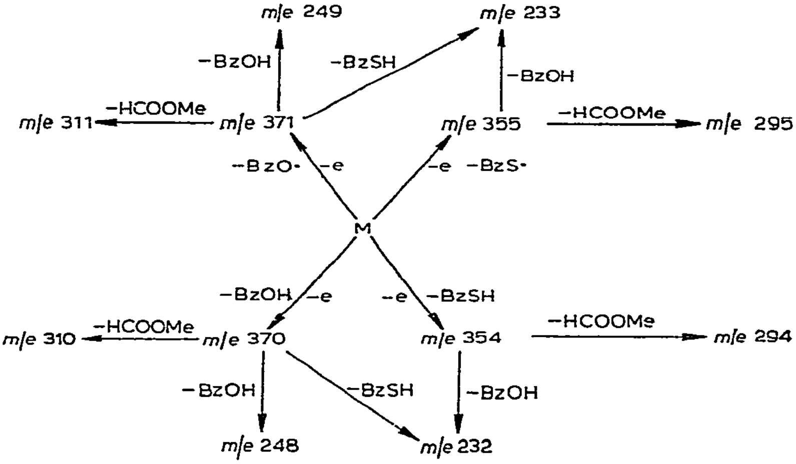
[*] When the fragmentation of compounds **3**, **5**, **7**, **9**, **12**, and **14** is discussed, the *m/e* values of the corresponding peaks in the spectra of the deuterated compounds **4**, **6**, **8**, **10**, **13**, and **15** are given in parentheses.

[**] For elucidation of the fragmentation of **12**, the mass spectra of 1,2-*O*-isopropylidene-α-D-xylofuranose (**14**) and its deutero analog were recorded and interpreted.

·OMe, ·OBz, and ·SBz radicals, or by the elimination of molecules BzOH, BzSH, BzOBz, or BzSBz. Through formation of ·OMe radical, a less distinct series is evolved that gives rise to ions at *m/e* 461, 339, 217, and 201:



The pathways of cleavage beginning by the elimination of BzO·, BzS·, BzOH, and BzSH continue through the elimination of HCOOMe, or BzOH or BzSH (see Scheme 3).



SCHEME 3

The ions on the left in Scheme 3 contain sulfur, and those on the right contain an atom of oxygen instead. The approximate ratio of the relative intensities of the peaks containing oxygen and sulfur (both are formed in the same way), namely, 355:371, 354:370, 295:311, 294:310, 233:249, and 232:248, as well as 201:217 in the preceding pathway, is 3:1. It follows from the foregoing that the (bulkier) thiobenzoyl group splits off three times more readily than the benzoyl group.

In another course of fission of molecular ions, a molecule of anhydride (BzOBz) or sulfide (BzSBz) is split off. The same phenomenon was observed and described[1]

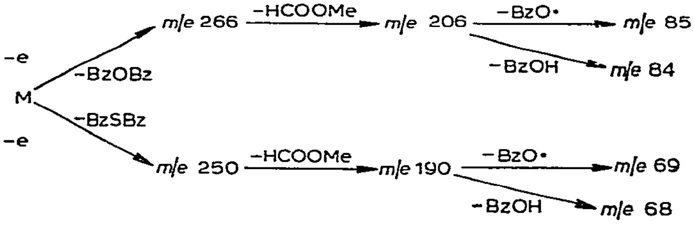


TABLE I

RATIOS OF MASS TO CHARGE, AND RELATIVE INTENSITIES IN THE MASS SPECTRA OF SOME 4-THIO-α-D-XYLOSE DERIVATIVES[a]

Compound 1		*Compound* 2		*Compound* 3		*Compound* 5		*Compound* 7		*Compound* 9		*Compound* 11		*Compound* 12		*Compound* 14	
m/e	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%
29	20	41	6	29	18	149	30	161	22	149	12	41	15	39	11	39	18
31	6	50	12	31	19	150	36	164	62	150	8	42	5	41	25	41	27
39	9	51	61	39	22	151	22	166	12	151	8	43	100	42	9	42	14
41	18	59	9	41	19	164	76	220	10	153	10	44	15	43	100	43	100
42	22	68	25	43	79	166	48	238	100	173	10	45	18	44	9	44	7
43	100	69	17	45	45	178	22	239	44	179	10	55	18	45	29	55	30
44	12	76	15	51	7	179	18	270	78	181	8	57	8	46	6	56	28
45	27	77	100	55	29	180	14	M	6	192	8	58	6	47	8	57	16
59	33	78	30	57	34	220	36			203	22	59	63	55	18	59	100
60	5	84	8	58	6	238	100			220	20	60	8	56	22	60	10
61	9	85	6	59	77	256	52			221	80	69	5	57	16	61	9
68	15	104	5	60	13	M	4			222	14	71	8	58	12	68	5
69	31	105	100	61	15					238	84	72	13	59	100	69	9
70	6	106	51	63	5					239	8	73	9	60	27	71	26
73	12	107	9	65	32					240	28	74	5	61	16	73	43
74	23	111	6	69	13					256	100	85	50	69	7	74	38
84	35	122	7	71	8					257	12	88	13	71	50	85	66
85	56	190	11	73	12					258	34	100	100	72	8	86	5
86	5	201	9	75	5					274	94	101	20	73	31	100	5
87	6	217	3	77	6					275	10	113	9	74	44	101	12
97	5	232	24	85	34					276	30	129	38	75	10	115	9
99	4	233	15	89	11					M	2	130	5	85	31	127	34
101	24	248	8	91	100							a31	9	89	18	159	24
102	46	294	100	92	43							158	19	100	41	175	100
103	26	295	72	100	100							173	13	101	100	176	8

104	5	296	13	101	31	188	4	102	9
113	9	310	32	117	5	231	24	103	6
115	10	311	23	121	7	246	24	129	9
116	7	339	4	122	79	M	2	130	8
127	7	354	1.6	123	39			131	13
128	9	355	1.5	124	29			143	40
129	62	370	0.6	133	8			148	45
130	9	461	1.2	137	6			149	6
131	22			150	6			191	41
139	10			164	50			192	6
144	49			165	8			193	6
155	6			166	7			206	35
157	8			178	11			207	5
170	13			189	9			M	4
171	100			220	13				
172	13			221	10				
173	14			238	71				
186	27			239	8				
187	13			240	5				
203	0.9			279	10				
204	7.5			294	4				
205	0.7			M	2				
206	0.6								
214	0.5								
215	5.4								
231	2.3								
246	2.6								
275	3.4								

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[a] Compound **1**, methyl 2,3-di-*O*-acetyl-4-*S*-acetyl-4-thio-α-D-xylopyranoside; **2**, methyl 2,3-di-*O*-benzoyl-4-*S*-benzyol-4-thio-α-D-xylopyranoside; **3**, 4-*S*-benzyl-1,2-*O*-isopropylidene-4-thio-α-D-xylose; **5**, 4-*S*-benzyl-4-thio-α-D-xylopyranose; **7**, methyl 4-*S*-benzyl-4-thio-α-D-xylopyranoside; **9**, 4-*S*-benzyl-3-chloro-3-deoxy-4-thio-α-D-xylopyranose; **11**, 1,2:3,5-di-*O*-isopropylidene-4-thio-α-D-xylofuranose; **12**, 1,2-*O*-isopropylidene-4-thio-α-D-xylo-uranose; and **14**, 1,2-*O*-isopropylidene-α-D-xylofuranose.

for the fragmentation of methyl 2,3-di-*O*-benzoyl-4-*O*-*p*-tolylsulfonyl-β-L-arabinopyranoside. The ratio of relative intensities of the peaks, namely, 190:206, 69:85, and 68:84, is 3:1; this indicates that the elimination of the sulfide (containing the bulky sulfur atom) also occurs three times faster than the elimination of BzOBz.

In the spectra of 4-thiobenzyl derivatives **3**–**10**, the most prominent peaks are those at *m/e* 91, corresponding to the tropylium ions, at *m/e* 65 (m* = 46.4; 91→65) and 39, and those of α-toluenethiol at *m/e* 124 (for the deuterated compounds, at 125). The ions at *m/e* 123, 122, and 45 are also quite pronounced (see Table I), and probably have the following structure (Ph = phenyl):

$\mathrm{Ph{-}CH{=}\overset{+}{S}H}$	$\mathrm{Ph{-}CH{=}\cdot\overset{+}{S}}$	$\mathrm{CH{\equiv}\overset{+}{S}}$
m/e 123	*m/e* 122	*m/e* 45

The presence of peaks at *m/e* 124, 123, 122, and 45 together with peaks at *m/e* 91, 65, and 39 can serve as a criterion of the presence of a thiobenzyl group in a molecule of a sugar derivative.

In the spectrum of 4-*S*-benzyl-1,2-*O*-isopropylidene-4-thio-α-D-xylopyranose **3** (see Table I) (and in the spectrum of its deutero analog **4**), a faint peak for molecular ions at *m/e* 296 (297) is present. At *m/e* 294 (295), there is a slightly more intense peak of the ions $(M-H_2)^+$. From these are produced the ions $(M-\cdot CH_3)^+$ at *m/e* 281 (282) and $(M\text{-}H_2-\cdot CH_3)^+$ at *m/e* 279 (280). The ions $(M-\cdot CH_3)^+$, after elimination of a molecule of CH_3COOH, give rise to the ions at *m/e* 221 (221). Through a different pathway of fragmentation, the $(M-CH_3COCH_3)^+$ ions are formed (m* = 119.3; 296→238). These are dehydrated, giving rise to the ions $(M-CH_3COCH_3-H_2O)^+$ at *m/e* 220 (220) (m* = 203.3; 238→220). The presence of intense peaks at *m/e* 100 and 85 (m* = 72.2; 100→85) proves the fission of the pyranose ring of the molecular ions common to isopropylidene derivatives of pyranoses[3], with the formation of ions containing two carbon atoms of the ring (C-1 and C-2, C-3 and C-4). As the peak at *m/e* 166 of the ions containing C-3 and C-4 with the corresponding substituents is imperceptible, whereas the peak at *m/e* 164 is quite pronounced, we assume that the ions at *m/e* 164 arise from the ions at *m/e* 166 by elimination of H_2. Thus, the conjugation of the benzene nucleus of the benzylthio group is realized. According to this presumption, as well as the fact that, in the deuterated compound, this peak is shifted to *m/e* 165, we suggest the following formulation of the ions at *m/e* 164 (165):

$$\mathrm{Ph{-}CH{=}\overset{+}{S}{-}\overset{\bullet}{C}{=}CH{-}OH}$$

m/e 164 (165)

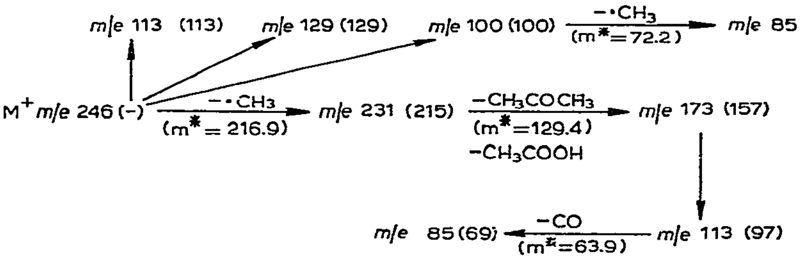
This formulation is in accord with the fact that the peak of the ions at *m/e* 164 (165) is present in the spectra of compounds **5**–**8** (containing a free hydroxyl group on C-3), but is not present in the spectra of the 3-chloro-3-deoxy sugars **9** and **10**.

The elimination of a molecule of water from the molecular ions of **5** (and **6**) at *m/e* 256 (259) results in the formation of the ions $(M\text{-}H_2O)^+$ at *m/e* 238 (240) (m* = 221.4; 256→238), which are further dehydrated, giving rise to the ions $(M-2H_2O)^+$ at *m/e* 220 (221) (see Table I).

From the molecular ions of methyl 4-*S*-benzyl-4-thio-α-D-xylopyranoside (**7**) (and **8**) (see Table I) at *m/e* 270 (272), a $\cdot OCH_3$ radical is cleaved off, with the formation of $(M - \cdot OCH_3)^+$ ions at *m/e* 239 (241). In addition, from the molecular ions, a molecule of methanol is eliminated, giving rise to the ions $(M - CH_3OH)^+$ at *m/e* 238 (240) (m* = 209.8; 270→238). The ions $(M - \cdot OCH_3)^+$, as well as the ions $(M - CH_3OH)^+$, are dehydrated and, hence, the ions at *m/e* 221 (222) and 220 (221) (m* = 203.3; 238→220) are originated. In the spectra of compounds **5**–**8**, the peaks at *m/e* 166 and 164, already discussed, are present.

The dehydration of the molecular ions of 4-*S*-benzyl-3-chloro-3-deoxy-4-thio-α-D-xylopyranose (**9**) at *m/e* 274 (for compound **10** at *m/e* 276) (see Table I) results in the formation of the ions $(M - H_2O)^+$ at *m/e* 256 (257) (m* = 239.2; 274→256 and m* = 241.3; 276→258 for the ions containing ^{37}Cl). Further dehydration of the ions $(M - H_2O)^+$ gives rise to the ions $(M - 2H_2O)^+$ at *m/e* 238 (238) (m* = 221.4; 256→238 and m* = 223.3; 258→240). In a different way, a $\cdot Cl$ radical is split off from the ions $(M - H_2O)^+$, and the ions $(M - H_2O - \cdot Cl)^+$ at *m/e* 211 (222) are formed. The ions $(M - H_2O - \cdot Cl - H_2O)^+$ at *m/e* 203 (203) could be formed by further dehydration of the ions at *m/e* 221.

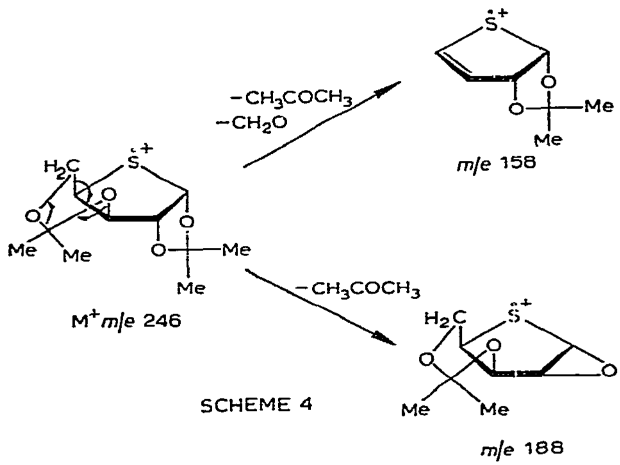
In contrast to the spectra of *O*-isopropylidenepentofuranoses[3], in which the molecular ion-peaks are not present, the spectra of *O*-isopropylidene-4-thio-D-xylofuranoses show pronounced molecular ion-peaks. Some of the pathways of fragmentation of the molecular ions of 1,2:3,5-di-*O*-isopropylidene-4-thio-α-D-xylofuranose (**11**) (see Table I) are the same as suggested by De Jongh and Biemann for 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose[3]. (The peaks present in the spectrum of the O-analog[3] are given in parentheses.)



The elimination of CO from the ions $(M - \cdot CH_3, CH_3COCH_3, CH_3COOH)^+$, which was previously substantiated for the fragmentation of methyl 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranuronate[4] is shown by the presence of a metastable peak.

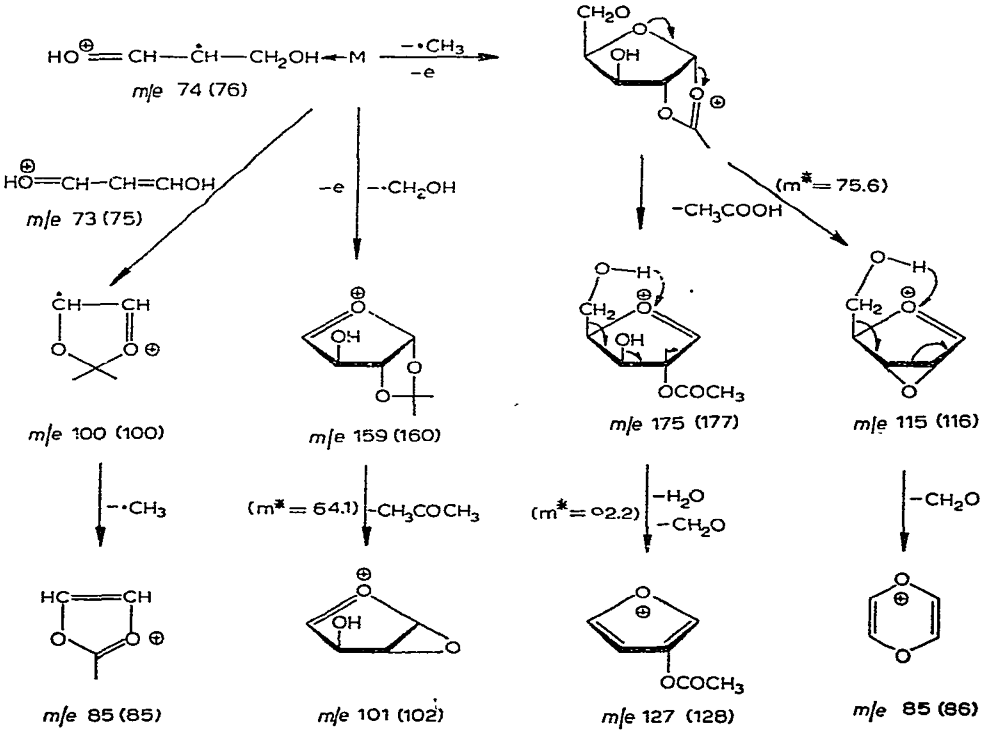
In addition to the ways of fragmentation already mentioned, the molecular ions are fragmented by two pathways in which the 1,3-dioxolane or *m*-dioxane ring is eliminated with the formation of $(M - CH_3COCH_3)^+$ ions at *m/e* 188 and $(M - CH_3COCH_3 - CH_2O)^+$ at *m/e* 158, respectively (see Scheme 4).

To elucidate the fragmentation of 1,2-*O*-isopropylidene-4-thio-α-D-xylofuranose (**12**), we examined the fragmentation of 1,2-*O*-isopropylidene-α-D-xylofuranose (**14**)



SCHEME 4

(see Table I). In the spectrum of **14**, the peak of the molecular ions is not found. As a methyl radical is split off, the ions $(M-\cdot CH_3)$ at *m/e* 175 (177) are observed, from which are formed, after elimination of water and formaldehyde, the ions $(M-\cdot CH_3 - H_2O - CH_2O)^+$ at *m/e* 127 (128) or, after elimination of acetic acid, the $(M-\cdot CH_3 - CH_3COOH)^+$ ions at *m/e* 115 (116). From the latter, a molecule of formaldehyde is eliminated, with the formation of ions at *m/e* 85 (86). In a different way, a $\cdot CH_2OH$



SCHEME 5

radical is cleaved from the molecular ion, giving ions $(M - \cdot CH_2OH)^+$ at *m/e* 159 (160); a molecule of acetone is eliminated, which gives rise to the ions $(M - \cdot CH_2OH - CH_3COCH_3)^+$ at *m/e* 101 (102). The ions containing two carbon atoms of the furanose ring with the respective substituents are shown by the peaks at *m/e* 100 (100), 74 (76), and 73 (75). The mechanism suggested for the fragmentation of **14** is given in Scheme 5. The values in parentheses are related to the deuterated compound **15**.

In the spectra of 1,2-*O*-isopropylidene-4-thio-α-D-xylofuranose (**12**) (see Table I) and **13**, an intense peak of molecular ions is present. As with its oxygen analog **14** (see Scheme 5), the disintegration of the molecular ions (**12**) is initiated by the splitting off of the $\cdot CH_3$ radical, producing ions at *m/e* 191 (193), 143 (144), 131 (132), and 101 (102). For both compound **12** and **14**, the peaks at *m/e* 100 (100), 85 (85), 74 (76), and 73 (75) represent ions containing C-1 and C-2, or C-3 and C-4. In contrast to the fragmentation of oxygen analog **14** (see Scheme 5), the pathway through which the radicals $\cdot CH_2OH$ are first eliminated does not occur Consequently, the peaks of the ions $(M - \cdot CH_2OH)^+$ and $(M - \cdot CH_2OH - CH_3COCH_3)^+$ are not present in the spectra of **12** (see Table I). On the other hand, in the spectra of **12** and **13**, there is an intense peak of $(M - CH_3COCH_3)^+$ ions at *m/e* 148 (150). Besides the inequality in the stability of the molecular ions, the splitting off of the radical $\cdot CH_2O$ from the molecular ions of the 4-*O* compound and the elimination of CH_3COCH_3 from the 4-*S* compound are the main differences in the mass-spectral behavior of compounds **12** and **14**.

EXPERIMENTAL

The experimental details have been described[1]. The temperature at the site of evaporation was 20–45°, and that in the ionizing chamber was 120–140°. The overall degrees of deuteration were:

4, 80; **6**, 56; **8**, 58; **10**, 70; **13**, 93; and **15**, 93%.

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