Carbohydrate Research, 31 (1973) 377–386

MASS SPECTROMETRY OF SULFUR-CONTAINING DERIVATIVES OF SUGARS

PART III*. FRAGMENTATION OF SOME 5-THIO-D-GLUCOPYRANOSE, 4-THIO-D-ARABINOFURANOSE, AND 3-THIO-D-ALLOFURANOSE DERIVATIVES†

VLADIMÍR KOVÁČIK, PAVOL KOVÁČ
Institute of Chemistry, Slovak Academy of Sciences, 80933 Bratislava (Czechoslovakia)
AND ROY L. WHISTLER
Department of Biochemistry, Purdue University, West Lafayette, Indiana 47907 (U. S. A.)
(Received August 7th, 1972; accepted for publication in revised form, August 8th, 1973)

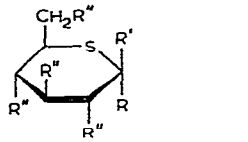
ABSTRACT

Mass spectra of several methyl and acetyl derivatives of 5-thio-D-glucopyranose, methyl derivatives of 4-thio-D-arabinofuranose, and acetyl and *O*-isopropylidene derivatives of 3-thio-D-allofuranose have been examined. Significant and diagnostic qualitative and quantitative differences in fragmentation of these derivatives compared to the corresponding oxygen analogs are discussed mainly from the point of view of the lower electronegativity of the sulfur atom compared to that of the atom of oxygen.

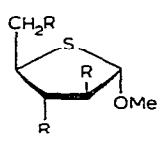
INTRODUCTION

Examination of fragmentation of numerous carbohydrate derivatives after electron impact[2,3] has convincingly shown the versatility of information that mass spectra can provide. Sulfur-containing sugars show expected but specific diagnostic patterns. In addition to different ionization potential[4], the roughly twofold total-ionization cross-section of sulfur-containing molecules compared to oxygen analogs[4] accounts for qualitative and quantitative differences in the fragmentation of molecular ions. As shown by early work[1,6], fragmentation of thio sugar derivatives differs from that of corresponding oxygen analogs. The aim of this work was to determine to what extent the well established[2,3,7–11] fragmentation mechanism of methyl ethers, acetates, and isopropylidene acetals of common sugars can be applied to similar sulfur-containing sugar derivatives. Model compounds selected for examination were several methyl and acetyl derivatives of 5-thio-D-glucopyranose, methyl ethers of 4-thio-D-arabinofuranose, and isopropylidene and acetyl derivatives of 3-thio-D-allofuranose.

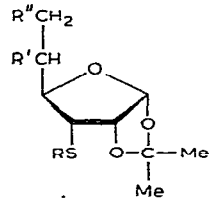
*For Part II, see Ref. 1.
†Journal Paper No. 4837 of the Purdue Agricultural Experimental Station, West Lafayette, Indiana 47907.



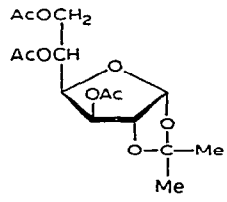
1 R = H, R′ = OMe, R″ = OMe
2 R = H, R′ = OMe, R″ = OH
2a R = H, R′ = OMe, R″ = OD
3 R = R′ = OH, H; R″ = OH
4 R = H, R′ = OMe, R″ = OAc
5 R = R′ = OAc, H; R″ = OAc



6 R = OMe
7 R = OH
7a R = OD



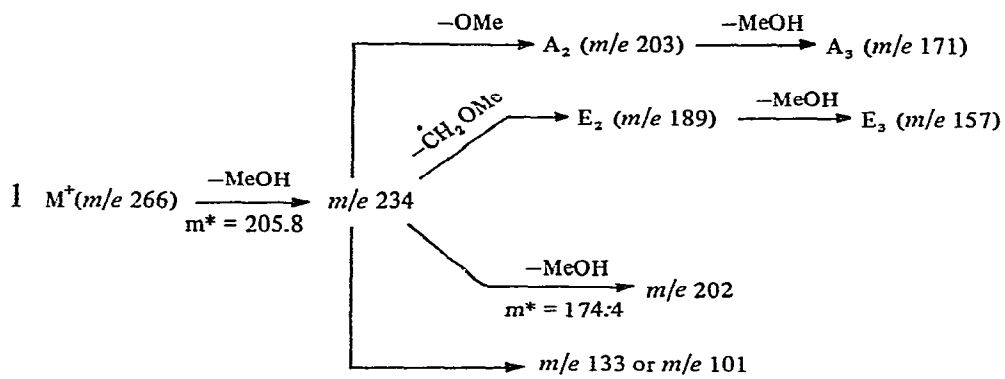
8 R = Ac, R′ = R″ = OH
8a R = Ac, R′ = R″ = OD
9 R = Ac, R′ = R″ = OAc
10 R = Ac; R′, R″ = O—Ip—O



11

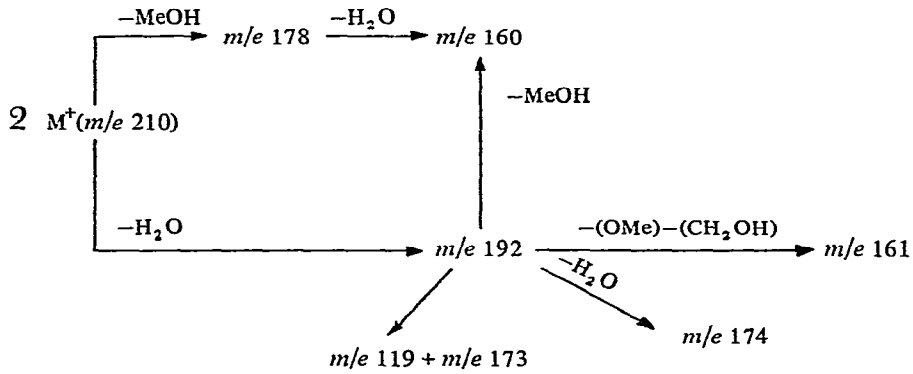
RESULTS AND DISCUSSION

The fragmentation of methyl 2,3,4,6-tetra-*O*-methyl-5-thio-β-D-glucopyranoside (**1**) differs in several ways from that of fully methylated methyl hexopyranosides[2,3]. Perhaps the most useful part of its mass spectrum (Table I) is the large molecular ion peak, which allows direct determination of the molecular weight. The smaller negative inductive effect of $-\dot{S}^+-$ ionoradicals, compared to that of $-\dot{O}^+-$ ionoradicals, on the neighboring C-5–C-6 and C-1–OMe bonds does not induce their cleavage in contrast to the splitting of common sugars which produce A_1 and E_1 ions. Instead, elimination of methanol takes place with the formation of $(M-32)^+$ ions not formed in the fragmentation of other permethylated hexopyranosides. The radicals $\cdot CH_2OMe$ and $\cdot OMe$ are then split off in the second stage of fragmentation to give rise to highly conjugated ions A_2 and E_2. Different modes of breakdown of



$(M-32)^+$ ions may give rise to the expulsion of another molecule of methanol or disproportionation to ions at *m/e* 101 or *m/e* 133. This fragmentation is likely to originate from $(M-32)^+$ glycal-type[12] ions. The disintegration of the thiopyranoide ring through a conjugated electronic shift and rearrangement processes produce, as in the case of fully methylated hexopyranosides[2,3], intense peaks of F_1 (G_1), H_1, J_1, H_2 and K_2 series at *m/e* 101, 88, 75, 73, and 71; $m^* = 60.6$ for $88 \rightarrow 73$. The

base peak in the spectrum of **1** at *m/e* 45 is that of the doublet of the ions $CH_2{=}\overset{+}{O}Me$ and $\overset{+}{C}H{=}S$.



In the fragmentation of methyl 5-thio-β-D-glucopyranoside (**2**) (Table I) similar differences, as compared to the fragmentation of methyl β-D-glucopyranoside[13], can be seen. The peaks of the A_1 and E_1 ions are missing in the spectrum of **2**. Abundant sulfur ions occur at *m/e* 87 and 73 (F_1, G_1), 74 and 60 (H_1), 59 (H_2) and 57 (K_2). The most abundant ions at *m/e* 77 have the structure $HS{=}{=}\overset{+}{C}H{=}{=}OMe$ which is exceptionally well stabilized by the mesomeric effect of S and O atoms. These ions are formed by relocation of a hydrogen atom, perhaps from the hydroxyl group at C-3, to the ring sulfur atom. The proposed structure and the mode of its formation is supported by the characteristic intensity of the peaks of the ions at *m/e* 79 containing ^{34}S in the spectrum of **2** and **7** (Table I), the value *m/e* 78 in the spectrum of *O*-deuterated compounds **2a** and **7a**, the absence of the peaks of the proposed structures in the spectra of methyl ethers **1** and **6** and in that of 5-thio-D-glucose (**3**). The mass spectrum of **3** (Table I) contains no peak of the molecular ion, which is dehydrated to give the ions $(M-18)^+$ at *m/e* 178. These, after having split off $\cdot CH_2OH$ or a molecule of water, give rise to the ions E_2 at *m/e* 147 and $(M-2\ H_2O)^+$ at *m/e* 160. As expected, the most abundant ions are those at *m/e* 73 and 60 (F_1 and H_1).

The influence of the sulfur atom is indicated also by the significant qualitative difference in the fragmentation by methyl 2,3,4,6-tetra-*O*-acetyl-5-thio-β-D-glucopyranoside (**4**) and 1,2,3,4,6-penta-*O*-acetyl-5-thio-D-glucopyranose (**5**) as compared to the fragmentation of common acetates[8,10]. As in the case of the just-discussed structures, no peaks of A_1 and E_1 series are present in the spectra of **4** and **5** (Table I). The smaller affinity of the sulfur atom for valency electrons as compared to the oxygen atom accounts for the lack of expulsion of HCSOMe or of HSOAc fragments from the molecular ions, which occurs when oxygen is present to give C_1 ions by elimination of HCO_2Me[8] or HCO_2Ac[9] fragments. This observation is in agreement

with the fragmentation of tetrahydropyran and thiacyclohexane[14] where a CH_2O fragment is easily split from the tetrahydropyran molecule, but expulsion of a CH_2S fragment from the thiacyclohexane molecule is negligible. Likewise, **5** does not disintegrate with formation of the ions $(M-Ac_2O-HCSOH)^+$ at *m/e* 242, that are abundant in the spectra of hexopyranose pentaacetates[10]. The fragmentation of

TABLE I

RATIOS OF MASS TO CHARGE (*m/e*) AND RELATIVE INTENSITIES (%) IN THE MASS SPECTRA OF 5-THIO-D-GLUCOPYRANOSE AND 4-THIO-D-ARABINOFURANOSE DERIVATIVES[a]

Compounds													
1		**2**		**3**		**4**		**5**		**6**		**7**	
m/e	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%
45	100.0	45	44.2	41	18.3	43	932.3	43	838.3	45	100.0	41	10.2
47	5.8	47	18.2	42	76.1	45	38.0	45	7.9	47	6.9	42	21.6
55	2.6	55	8.4	43	71.8	55	7.7	55	2.8	55	4.4	43	38.7
57	1.7	57	33.7	45	87.3	57	11.5	57	2.8	58	4.7	45	100.0
58	5.2	59	30.5	47	46.5	59	15.4	58	3.8	59	9.7	47	56.7
59	7.1	60	63.2	55	28.2	60	5.8	59	4.8	61	4.0	55	22.1
60	7.5	61	13.7	57	36.6	61	7.4	60	4.0	69	3.1	57	57.0
71	16.5	69	7.4	58	18.3	69	33.8	61	4.6	71	11.7	58	18.6
73	13.3	70	16.8	59	60.6	70	15.8	69	6.4	73	14.8	59	82.6
75	66.9	71	9.5	60	100.0	73	9.7	71	4.0	75	36.5	60	25.5
83	26.0	73	31.6	61	31.0	74	39.0	73	11.4	85	4.9	61	39.5
85	18.5	74	74.0	71	19.7	75	7.8	76	1.3	88	45.4	71	9.4
87	2.8	75	14.7	73	70.4	76	5.9	81	4.3	89	7.3	73	56.5
88	92.7	77	100.0	74	7.2	77	7.8	85	9.4	101	43.0	74	99.0
90	9.0	78	3.8	76	7.2	81	7.8	86	2.6	102	6.7	75	23.5
101	40.4	79	4.2	77	6.8	85	39.2	87	3.9	114	1.2	76	28.2
102	4.8	85	21.1	85	7.6	87	33.3	89	1.6	115	4.3	77	99.0
115	2.5	87	33.3	87	6.8	89	3.9	97	11.0	117	1.2	78	3.7
117	1.1	89	9.5	89	12.3	97	29.4	98	2.7	119	1.2	79	4.1
118	1.6	101	12.3	97	2.8	98	9.8	99	3.8	127	1.3	85	8.3
119	1.2	103	16.5	98	2.4	99	7.9	101	12.0	131	0.9	87	21.5
127	2.1	115	2.5	101	10.1	101	9.9	102	6.7	133	0.7	89	33.8
128	1.6	116	6.7	102	3.4	102	7.9	103	8.9	134	0.9	90	20.8
131	4.2	118	18.9	113	1.5	103	34.0	113	31.2	145	1.3	101	8.4
132	4.0	119	15.4	116	1.0	113	21.7	114	34.2	157	2.4	102	9.4
133	14.6	127	2.0	119	3.4	114	25.6	115	12.5	159	6.8	103	21.4
145	1.0	129	3.1	127	1.1	115	21.7	125	8.5	160	0.8	117	10.1
146	1.1	130	2.0	129	2.3	118	13.8	129	19.8	177	0.4	118	6.0
147	1.0	131	1.8	131	1.0	125	11.8	131	4.0	190	6.5	131	4.9
157	0.8	132	1.4	147	3.0	127	7.9	142	69.8	191	0.9	132	4.0
158	0.9	133	2.8	160	1.0	129	9.9	143	19.0	222	0.1	144	7.5
160	2.0	142	1.1	178	0.6	142	23.1	144	3.5	M^+		145	8.9
171	0.9	143	1.1	$(M-18)^+$		143	79.1	155	11.9			148	1.0
176	0.4	144	1.2			144	9.9	156	2.0			149	2.5
189	2.3	148	0.9			145	9.2	169	1.6			162	40.8
202	0.4	160	2.3			156	12.6	171	16.3			180	2.8
203	0.3	161	6.3			157	73.8	173	2.4			M^+	

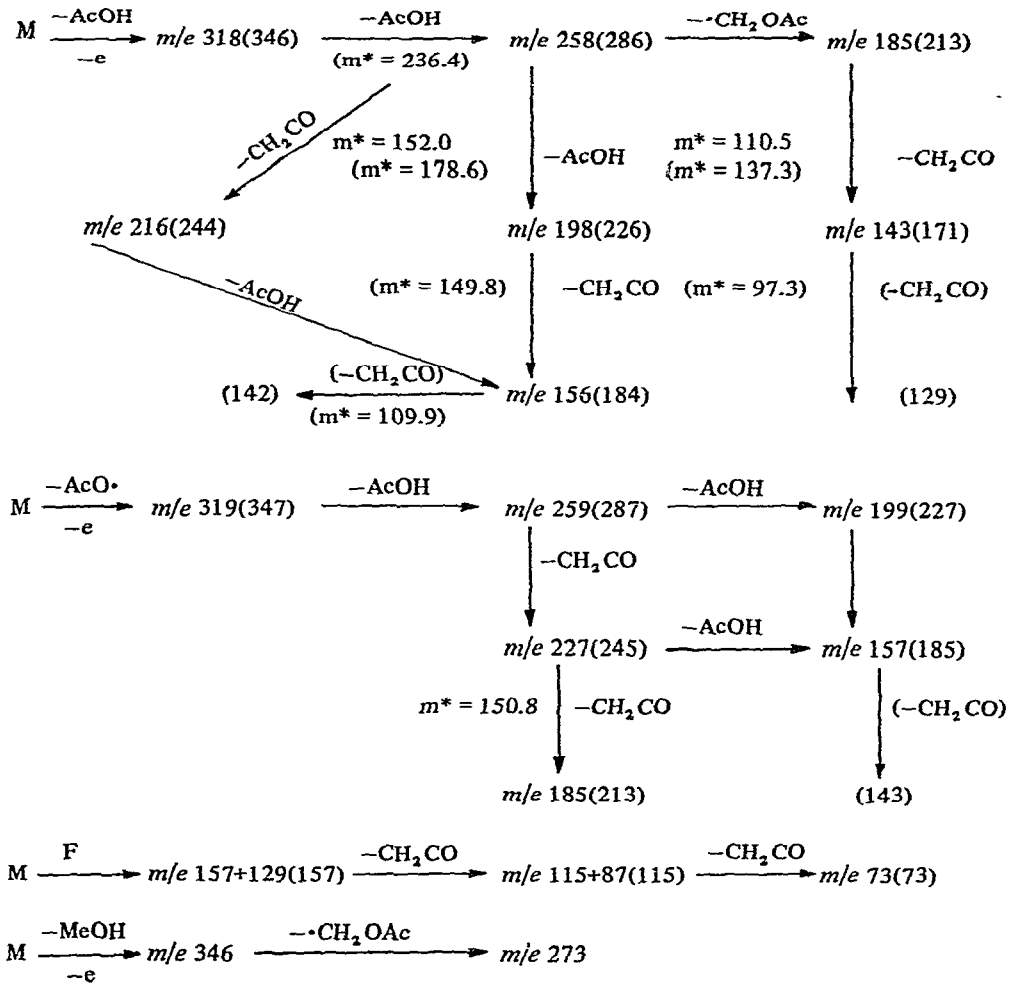
TABLE 1 (*continued*)

Compounds													
1		**2**		**3**		**4**		**5**		**6**		**7**	
m/e	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%
234	2.1	174	1.8			158	27.0	184	72.3				
235	0.1	178	2.9			174	6.7	185	100.0				
266	3.7	192	4.7			175	4.7	186	13.4				
$M^{\ddagger}$		210	4.7			183	11.4	202	5.9				
		$M^{\ddagger}$				184	18.5	213	8.6				
						185	100.0	226	17.4				
						198	41.7	227	43.6				
						199	67.5	228	5.6				
						215	24.8	244	3.9				
						216	13.6	245	3.8				
						227	18.3	286	2.3				
						258	7.8	346	0.3				
						259	2.2	347	0.4				
						273	0.3	$(M-59)^+$					
						318	0.3						
						319	0.3						
						346	0.1						
						$(M-32)^+$							

[a]Compound **1**, methyl 2,3,4,6-tetra-*O*-methyl-5-thio-β-D-glucopyranoside; **2**, methyl 5-thio-β-D-glucopyranoside; **3**, 5-thio-D-glucopyranose; **4**, methyl 2,3,4,6-tetra-*O*-acetyl-5-thio-β-D-glucopyranoside; **5**, 1,2,3,4,6-penta-*O*-acetyl-5-thio-D-glucopyranose; **6**, methyl 2,3,5-tri-*O*-methyl-4-thio-α-D-arabinofuranoside; **7**, methyl 4-thio-α-D-arabinofuranoside.

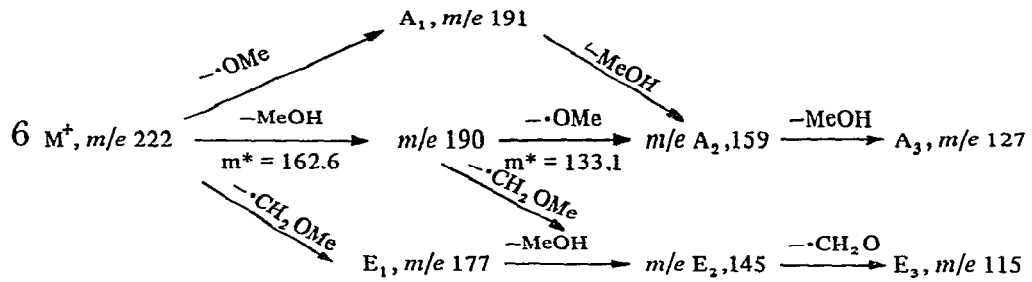
4 and **5** proceeds in three general ways (Scheme 1). Elimination of acetic acid from the molecular ion produces the ion at *m/e* 318 (346). The numbers in parentheses indicate the *m/e* values of the ions from fragmentation of **5**. The ion $(M-60)^+$ does not disintegrate with the elimination of CHSOMe or CHSOAc, as would be expected by analogy with methyl per-*O*-acetylhexopyranosides[2]. After elimination of an additional molecule of acetic acid, the ion disintegrates either with the removal of $\cdot CH_2OAc$ radicals or by elimination of AcOH or CH_2CO molecules. Cleavage of ·OAc from the molecular ion gives rise to the ion at *m/e* 319 (347) which, after elimination of AcOH or CH_2CO, further disintegrates. The ion at *m/e* 259 (287) might, however, have originated from the ions $(M-AcOH)^+$ after cleavage of an OAc radical.

The ion at *m/e* 157 (also the ion at *m/e* 129 in compound **4**) and the disintegration products are analogous to the ions F_1 produced by the fragmentation of pyranose pentaacetates[8–10]. In addition, the spectrum of glycoside **4** contains an intense peak H_1 at *m/e* 74 and a faint peak at *m/e* 346. The latter, which represents the ion $(M-MeOH)^+$, further disintegrates with the formation of the ion at *m/e* 273, after elimination of a $\cdot CH_2OAc$ radical.



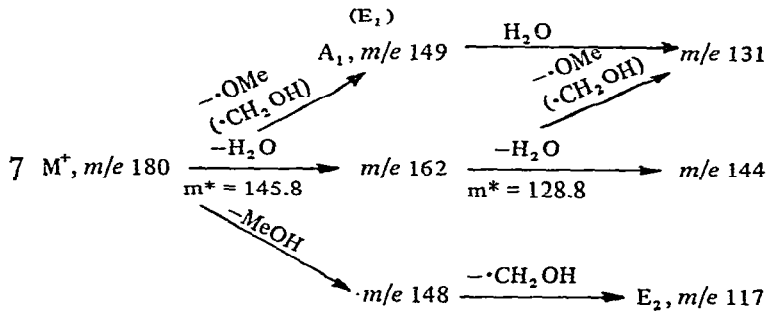
Scheme 1.

As can be seen from the spectrum of methyl 2,3,5-tri-*O*-methyl-4-thio-α-D-arabinofuranoside (**6**) (Table I) fragmentation of permethylated 4-thiofuranosides differs again markedly from the fragmentation of furanosides of common methylated sugars[2,3,7]. The elimination of methanol is preferred to the formation of A_1 and E_1 ions which are produced in minor amounts. Ions A_2 and E_2 are formed mainly after elimination of CH_2OMe or ·OMe radicals from $(M-32)^+$ ions. Here again the lack of HCSOMe elimination from the molecular ions, which would be analogous to the elimination of HCO_2Me from the molecular ions of permethylated pentofuranosides[7,15] to produce the C_1 ions, can be explained by the lower electronegativity of the sulfur atom. Similar features can be found when comparing the mass spectrum of tetrahydrofuran to that of tetrahydrothiophene[16]. No peaks correspond-



ing to the intense peaks of the ions $(M-CH_2O)^+$ present in the spectrum of the former compound can be found in the spectrum of the latter compound. The order of decreasing relative intensity of the most abundant ions at *m/e* 45, 88 (H_2), 101 (G_1), 75 (J_1), 73 (H_2) and (K_2) differs from that of O-analogs which is in the order: 101, 45, 75, 88, and 71. Peaks of H_1 ions are quite intense in the spectrum of compound **5**.

Dehydration of the molecular ions, which is not observed in the fragmentation of methyl pentofuranosides[15], is prominent in the fragmentation of methyl 4-thio-α-D-arabinofuranoside (**7**) (Table I). The ions at *m/e* 77 (at *m/e* 78 after deuteration in the spectrum of **7a**) and some at *m/e* 45 contain sulfur, whereas the other intense peaks at *m/e* 74 (H_1), 87 and 73 (G_1), 61 (J_1), and 59 (H_2) are prominent in the corresponding O-analog[15]. The abundance of the ions of the H series is again noted.



For the elucidation of the fragmentation of compounds **8–10**, the mass spectrum of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**11**) was recorded and interpreted.

Whereas the mass spectra of 1,2-*O*-isopropylidene derivatives of 4-thio-D-xylofuranose[1] and 5,6-epithio-D-glucofuranose[10] contain intense peaks of the molecular ions, the peaks of the molecular ions were not found in the spectra of 3-*S*-acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose derivatives (Table II). The highest peak is that of $(M-15)^+$ ions. Disintegration of the molecular ions of 3-*S*-acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose (**8**) proceeds by cleavage in the exocyclic portion of the molecule through E splitting and gives rise to the ions at

TABLE II

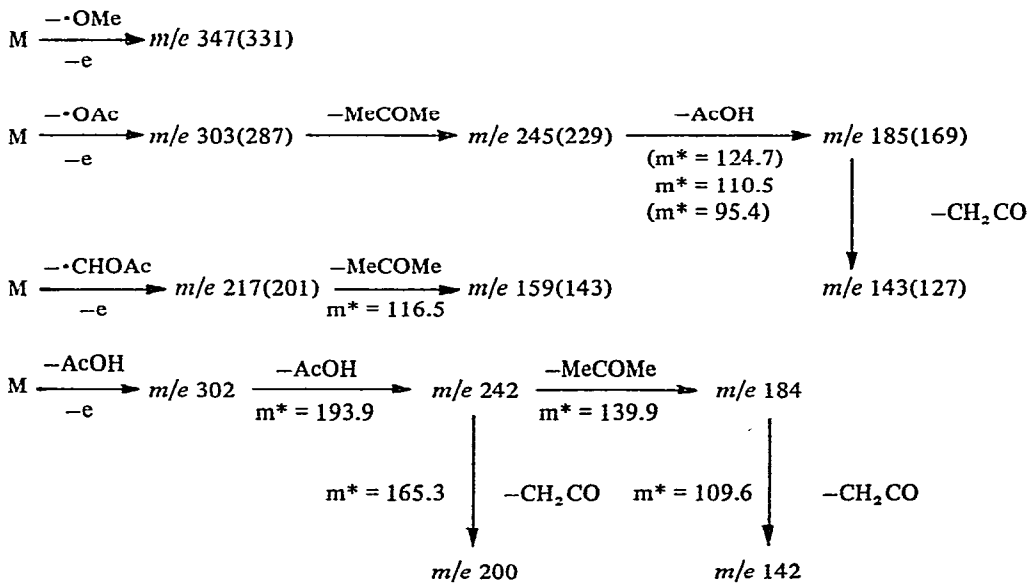
RATIOS OF MASS TO CHARGE (*m/e*) AND RELATIVE INTENSITIES (%) IN THE MASS SPECTRA OF 3-THIO-α-D-ALLOFURANOSE DERIVATIVES AND OF 3,5,6-TRI-*O*-ACETYL-1,2-*O*-ISOPROPYLIDENE-α-D-GLUCOPYRANOSE[a]

Compounds							
8		**9**		**10**		**11**	
m/e	%	*m/e*	%	*m/e*	%	*m/e*	%
43	874.1	43	1250.0	43	314.8	43	320.4
45	29.6	45	14.8	45	9.2	45	6.4
55	15.6	55	17.4	55	9.4	55	15.3
57	15.7	57	7.3	57	3.8	59	35.3
58	14.1	58	8.3	58	4.7	61	6.0
59	125.9	59	88.3	59	37.5	68	6.4
60	13.0	61	5.7	61	4.6	69	9.8
61	34.0	69	7.6	69	3.7	71	8.9
69	22.0	71	5.1	71	3.5	73	26.0
71	9.3	73	11.7	72	8.9	81	26.0
73	14.6	81	30.7	73	9.3	85	58.7
81	14.6	84	38.5	81	5.8	86	16.6
85	35.8	85	25.5	85	10.0	97	20.9
87	25.9	87	30.9	87	9.7	98	13.2
88	10.6	89	21.4	89	2.5	99	10.6
89	46.9	97	19.5	101	100.0	100	7.7
97	8.7	99	9.4	102	5.7	101	23.0
99	11.1	101	17.0	113	4.2	103	14.5
113	12.0	102	21.9	115	7.5	109	53.6
115	7.4	113	16.1	117	5.9	113	8.9
117	13.0	115	31.3	125	3.9	115	58.7
127	14.3	117	13.3	127	3.7	126	10.2
129	7.8	125	9.4	129	1.3	127	50.2
131	18.6	127	8.9	131	2.0	128	15.7
159	100.0	129	5.7	143	17.2	129	9.4
160	9.6	131	12.5	159	41.3	139	10.2
161	7.0	142	33.1	160	3.3	141	11.2
173	2.1	143	16.5	161	2.1	143	56.2
175	2.2	159	100.0	185	5.8	145	10.6
177	7.6	169	5.1	202	3.3	155	5.9
187	3.4	184	8.4	203	2.0	157	12.8
189	7.4	185	7.9	217	5.9	169	100.0
203	4.0	200	6.5	245	3.4	170	12.5
217	16.3	217	29.7	259	1.3	198	12.3
263	10.7	229	2.3	303	47.2	201	7.5
$(M-15)^+$		242	7.6	$(M-15)^+$		202	3.7
		245	10.8			211	3.7
		257	1.0			215	5.4
		273	1.8			217	13.8
		302	1.3			226	5.4
		303	1.6			255	2.0
		347	13.5			271	0.6
		$(M-15)^+$				287	1.1
						331	84.3
						$(M-15)^+$	

[a]Compound **8**, 3-*S*-acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose; **9**, 5,6-di-*O*-acetyl-3-*S*-acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose; **10**, 3-*S*-acetyl-1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-allofuranose; and **11**, 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose.

m/e 61 (at *m/e* 63 after deuteration) and at *m/e* 217. The fact that a molecule of acetone is liberated from the latter ion is proved by the detection of the corresponding metastable ions (m* = 116.5) for *m/e* 217 → 159. Elimination of acetone from the molecular ions, typical of 1,2-*O*-isopropylidene-4-thio-D-xylofuranose[1], does not occur.

Very few qualitative differences were found when comparing the fragmentation of 5,6-di-*O*-acetyl-3-*S*-acetyl-1,2-*O*-isopropylidene-3-thio-α-D-allofuranose (**9**) with that of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**11**) (Table II). Fragmentation is initiated by the cleavage of ·OMe and ·OAc radicals and of the side chain of the ring. A molecule of acetic acid is liberated from the molecular ion of the 3-thio compound to form a new fragmentation series (Scheme 2), as shown in the spectrum of **11**. Elimination of the thiolacetate group as AcSH is not observed. The disproportionation of this group in the last stage of fragmentation is shown by the elimination of ketene.



Scheme 2.

Fragmentation of 3-*S*-acetyl-1,2:5,6-di-*O*-isopropylidene-3-thio-α-D-allofuranose (**10**) occurs in two main reactions. The first is the cleavage of the exocyclic part of the molecule with the formation of ions at *m/e* 101 or 217, and the second is the disintegration of $(M-\cdot CH_3)^+$ ions. The absence of molecular ion peaks in the spectra of **8–10**, suggests that the sulfur atom at C-3, is no longer the center of ionization. As with other cyclic sugar derivatives, the hemiacetal oxygen atom has become the center of ionization.

10 $M \xrightarrow[-e]{} m/e\ 101 \text{ or } 217 \xrightarrow[m^*=116.5]{-MeCOMe} m/e\ 159$

$M \xrightarrow[-e]{-\cdot CH_3} m/e\ 303 \xrightarrow[m^*=198.1]{-MeCOMe} m/e\ 245 \xrightarrow[m^*=139.7]{-AcOH}$

$m/e\ 185 \xrightarrow[m^*=110.5]{-CH_2CO} m/e\ 143$

EXPERIMENTAL

The experimental details have been described earlier[3]. The evaporation temperature was 25–65° and the temperature in the ionizing chamber 120–130°. The degrees of deuteration were 75% for **2a**, 95% for **7a**, and 55% for **8a**. When the origin of the ions could be explained by the mechanisms known from the fragmentation of common sugar derivatives, the ion nomenclature introduced by Kochetkov and Chizhov[3] was used.

ACKNOWLEDGMENT

The authors thank Mr. S. Markovič for skillful technical assistance.

REFERENCES

1 V. KOVÁČIK, P. KOVÁČ, AND R. L. WHISTLER, *Carbohyd. Res.*, 16 (1971) 353.
2 K. HEYNS, H. F. GRÜTZMACHER AND H. SCHARMANN, *Fortschr. Chem. Forsch.*, 5 (1966) 448.
3 N. K. KOCHETKOV AND O. S. CHIZHOV, *Methods Carbohyd. Chem.* (1972) 540.
4 R. W. KISER, *Introduction to Mass Spectrometry*, Prentice-Hall, Englewood Cliffs, N. J., 1965, p. 300.
5 H. BUDZIKIEWICZ, C. DJERASSI, AND D. H. WILLIAMS, *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco, 1967, p. 276.
6 K. HEYNS AND D. MULLER, *Tetrahedron*, 21 (1965) 3151.
7 N. K. KOCHETKOV AND O. S. CHIZHOV, *Tetrahedron*, 21 (1965) 2029.
8 D. C. DEJONGH AND K. BIEMANN, *J. Amer. Chem. Soc.*, 85 (1963) 2289.
9 K. BIEMANN, D. C. DEJONGH, AND H. K. SCHNOES, *J. Amer. Chem. Soc.*, 85 (1963) 1763.
10 K. HEYNS AND D. MÜLLER, *Tetrahedron Lett.*, 48 (1966) 6061.
11 D. C. DEJONGH AND K. BIEMANN, *J. Amer. Chem. Soc.*, 86 (1964) 67.
12 V. KOVÁČIK, V. BÍLIK, AND Š. KUČÁR, *Chem. Zvesti*, 24 (1970) 52.
13 P. A. FINAN, R. I. REED, W. SNEDDEN, AND J. M. WILSON, *J. Chem. Soc.*, (1963) 5945.
14 E. STENHAGEN, S. ABRAHAMSSON, AND F. W. MCLAFFERTY, *Atlas of Mass Spectra Data*, Vol. 1, Interscience, Philadelphia, 1969.
15 V. KOVÁČIK AND P. KOVÁČ, *Carbohyd. Res.*, 24 (1972) 23.
16 A. M. DUFFIELD, H. BUDZIKIEWICZ, AND C. DJERASSI, *J. Amer. Chem. Soc.*, 87 (1965) 2920.