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Note

Gas-liquid chromatography and mass spectrometry of trimethylsilyl ethers and butaneboronate–trimethylsilyl derivatives of polyhydroxyalkylpyrazines

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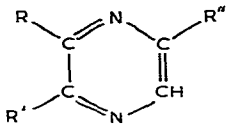
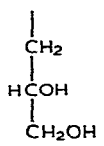
It is generally known that sugars react with ammonia to produce pyrazine compounds[1]. At least fifteen sugar-derived alkylpyrazines have been identified[2,3]. Only the following polyhydroxyalkylpyrazines, however, have been identified: 5-(D-*arabino*-tetrahydroxybutyl)-2-methylpyrazine[4], 6-(D-*arabino*-tetrahydroxybutyl)-2-methylpyrazine[4], 5-(D-*arabino*-tetrahydroxybutyl)-3-(D-*erythro*-trihydroxypropyl)-2-methylpyrazine[5], 2-(D-*arabino*-tetrahydroxybutyl)-5-(D-*erythro*-2,3,4-trihydroxybutyl) pyrazine (deoxyfructosazine)[6,8], 2-(D-*arabino*-tetrahydroxybutyl)-6-(D-*erythro*-2,3,4-trihydroxybutyl)pyrazine[7,8], 2,5-di-(D-*arabino*-tetrahydroxybutyl)pyrazine (fructosazine)[9–11], 2-(D-*glycero*-2,3-dihydroxypropyl)-5-(D-*threo*-trihydroxypropyl)pyrazine[12], 2-(D-*glycero*-2,3-dihydroxypropyl)-6-(D-*threo*-trihydroxypropyl)pyrazine[12,13], 2,5-di-(D-*threo*-trihydroxypropyl)pyrazine[14] and 2,6-di-(D-*threo*-trihydroxypropyl)-pyrazine[14].

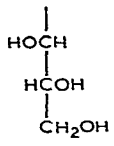
Our studies on the formation of polyhydroxyalkylpyrazines from the reaction of sugars with ammonia in weakly acidic medium showed that two (1-deoxypolyhydroxyalkyl)pyrazine isomers, such as deoxyfructosazine and its 6-isomer, were abundantly formed, but other homologues were detected only in trace amounts. However, in an alkaline medium, several kinds of unknown polyhydroxyalkylpyrazines were produced, probably from alkaline degradation-products of reducing sugars[15].

Hitherto, paper chromatography[4,8] and ion-exchange chromatography[8] have been used to separate and identify polyhydroxyalkylpyrazines. As it is difficult to separate individual compounds from a mixture containing several homologous members by these techniques, a combination of these methods with g.l.c.–m.s. analysis was investigated. Although a number of g.l.c.–m.s. analyses of trimethylsilyl ethers and butaneboronate–trimethylsilyl derivatives of carbohydrates and glycitols have been reported[16–21], corresponding data for derivatives of polyhydroxyalkylpyrazines have not been published.





a



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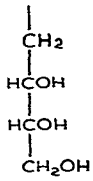

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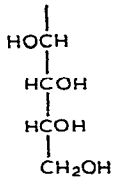


d

1 R = H , R′ = Me , R″ = d
2 R = Me , R′ = H , R″ = d
3 R = H , R′ = a , R″ = b
4 R = a , R′ = H , R″ = b
5 R = H , R′ = b , R″ = b
6 R = b , R′ = b , R″ = H
7 R = H , R′ = c , R″ = d
8 R = c , R′ = H , R″ = d
9 R = H , R′ = d , R″ = d

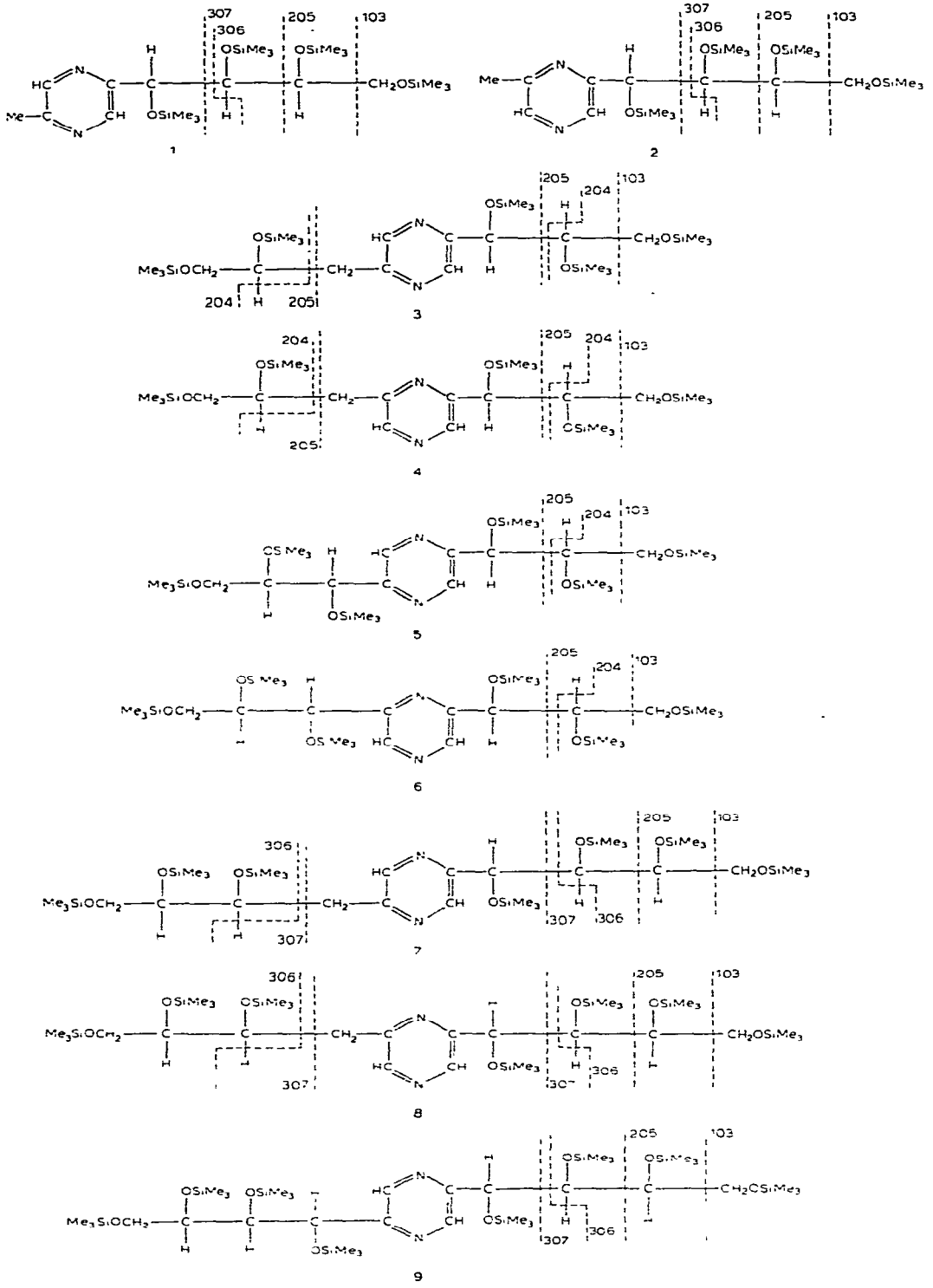
The trimethylsilyl ethers and butaneboronate–trimethylsilyl derivatives of the nine polyhydroxyalkylpyrazines **1–9** were prepared, and these derivatives were examined by g.l.c. The trimethylsilyl ethers gave, respectively, a single peak on chromatogram, and the retention time of each peak was different (Table I). On the other hand, the butaneboronate–trimethylsilyl derivatives showed some minor peaks, in addition to the main peak, except three perbutaneboronates of **1**, **2**, and **9** (Table I), which are devoid of trimethylsilyl groups.

TABLE I

RETENTION TIMES OF TRIMETHYLSILYL ETHERS AND BUTANEBORONATE–TRIMETHYLSILYL DERIVATIVES OF POLYHYDROXYALKYLPYRAZINES

Polyhydroxyalkyl-pyrazines	*Retention time of derivatives (min)*	
	Me_3Si	*$BuBO_3$–Me_3Si*
5-(D-*arabino*-Tetrahydroxybutyl)-2-methyl- (**1**)	5.50	4.25
6-(D-*arabino*-Tetrahydroxybutyl)-2-methyl (**2**)	5.27	4.25
2-(D-*glycero*-2,3-Dihydroxypropyl)-5-(D-*threo*-trihydroxypropyl)- (**3**)	11.40	9.25[a], 8.10
2-(D-*glycero*-2.3-Dihydroxypropyl)-6-(D-*threo*-trihydroxypropyl)- (**4**)	10.25	8.00[a], 7.25
2,5-Di-(D-*threo*-trihydroxypropyl)- (**5**)	12.40	11.25[a], 13.10
2,6-Di-(D-*threo*-trihydroxypropyl)- (**6**)	11.50	10.25[a], 11.75
2-(D-*arabino*-Tetrahydroxybutyl)-5-(D-*erythro*-2,3,4-trihydroxybutyl)- (**7**)	15.65	15.50[a], 15.20
2-(D-*arabino*-Tetrahydroxybutyl)-6-(D-*erythro*-2.3.4-trihydroxybutyl)- (**8**)	15.42	14.25[a], 13.96
2,5-Di-(D-*arabino*-tetrahydroxybutyl)- (**9**)	16.62	17.50

[a]Main peak.



Scheme 1. Fragmentation patterns of the trimethylsilyl ethers of 1–9.

The trimethylsilyl and butaneboronate–trimethylsilyl derivatives of **1–9** were subjected to g.l.c.–m.s. analysis. The mass spectral data of the trimethylsilyl derivatives showed the typical fragmentation of pertrimethylsilyl ethers of polyhydroxyalkyl chains and stability of the pyrazine nucleus towards electron bombardment (see Scheme 1), the major fragment ions being formed by the cleavage of the pertrimethylsilyl ethers of polyhydroxyalkyl chains (Tables II–VI). The main peaks are those formed by assuming β-cleavage of the polytrimethylsilyloxyalkyl chain; for the trimethylsilyl derivatives of **3**, **4**, **5** and **6**, ions at *m/e* 205 and *m/e* (M−204) are abundant, and for the trimethylsilyl derivatives of **1**, **2**, **7**, **8**, and **9**, ions at *m/e* 217, *m/e* 307, and *m/e* (M−306) are the main fragments. It is not possible to assert whether those main peaks are formed by a McLafferty rearrangement rather than by a simple β-cleavage. A γ-fission is reflected by the presence of ions at *m/e* (M−103) (for the trimethylsilyl derivatives of **3**, **4**, **5**, and **6**) and *m/e* (M−205) (for the trimethylsilyl derivatives of **1**, **2**, **7**, **8** and **9**), whereas α-fission-fragments are not evident.

TABLE II

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE TRIMETHYLSILYL ETHERS OF **1** AND **2**

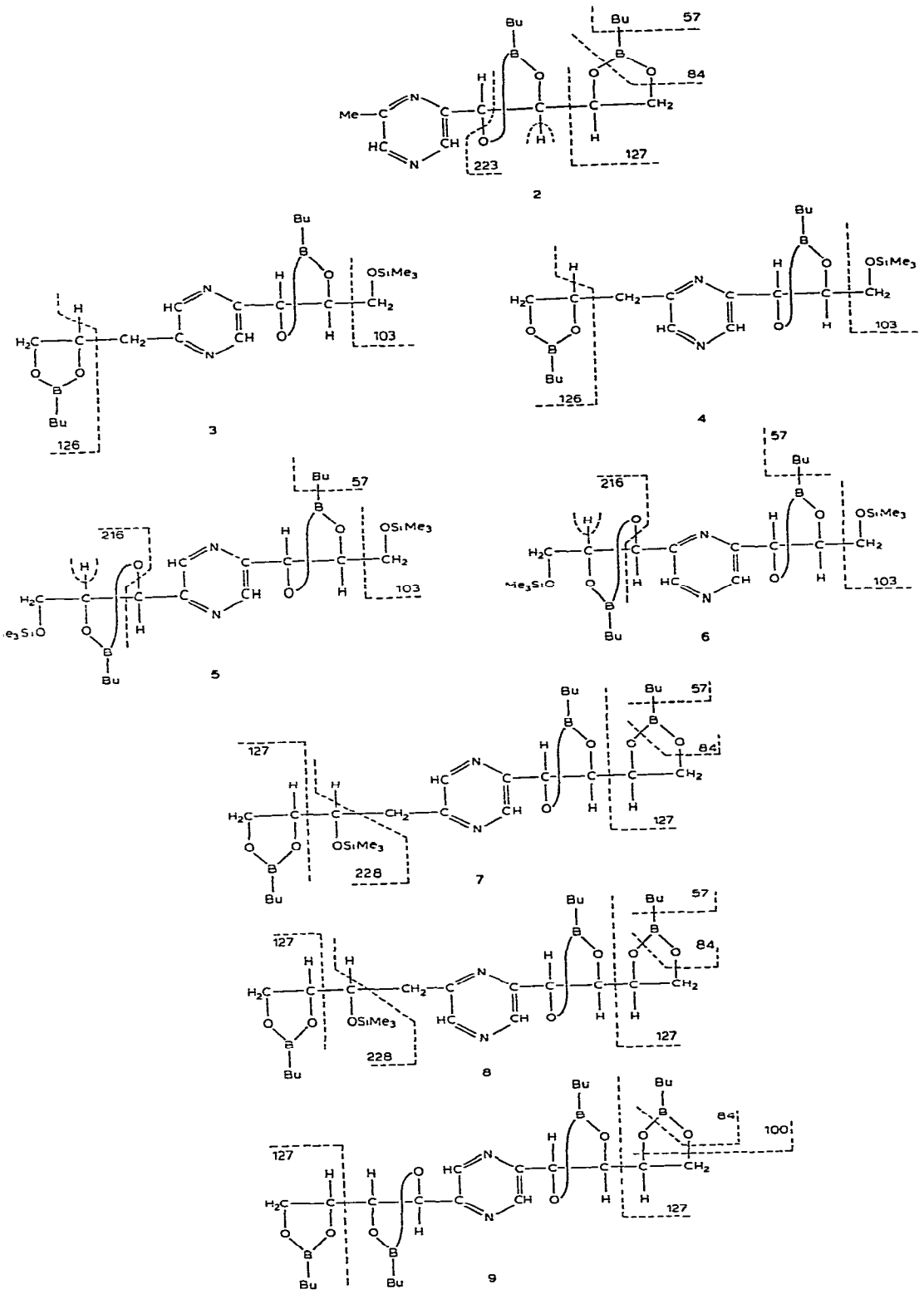
m/e	*Intensity* (%)				*Assignments*
	Me_3Si ether of **1**		*Me_3Si ether of* **2**		
	20 eV	*70 eV*	*20 eV*	*70 eV*	
502	28.7	5.0	12.2	4.1	M^+
487	11.9	2.6	7.8	3.4	$M-\overset{+}{C}H_3$
323	55.5	1.5	5.2	1.4	$M-(Me_3SiOH+Me_3SiO^+)$
307	100.0	25.2	63.9	18.8	$CH_2(OSiMe_3)-CH(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
297	5.9		5.7		$M-CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
277	12.9	2.7	13.9	3.4	*m/e* 307 $-2\overset{+}{C}H_3$
268	32.7	15.5	31.7	8.6	$M-[CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)+\overset{+}{C}_2H_5]$
217	63.4	34.5	76.1	21.0	$CH(OSiMe_3)=CH-\overset{+}{C}H(OSiMe_3)$
205	10.9	7.3	10.9	3.4	$CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
196	54.5	5.7	21.7	6.0	$M-CH(OSiMe_3)=C(OSiMe_3)-CH_2(OSiMe)$
189	13.9	5.6	8.7	3.0	$CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe)=CH_2$
147	6.9	21.6	16.1	17.8	$Me_3Si-O-\overset{+}{S}iMe_2$
103	90.7	60.8	100.0	42.2	$Me_3SiO\overset{+}{C}H_2$
73	12.9	100.0	22.6	100.0	$Me_3\overset{+}{S}i$

TABLE III

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE TRIMETHYLSILYL ETHERS OF **3** AND **4**

m/e	*Intensity* (%)				*Assignments*
	Me_3Si ether of **3**		*Me_3Si ether of* **4**		
	20 eV	*70 eV*	*20 eV*	*70 eV*	
604	37.4	4.8	23.0	4.2	M
589	24.2	6.0	10.0	2.9	$M-\overset{+}{C}H_3$
514	8.0	1.2	3.3	0.4	$M-Me_3SiOH$
501	7.7	2.0	5.3	0.9	$M-Me_3SiO\overset{+}{C}H_2$
472	10.5	2.4	13.8	2.9	$M-[Me_3SiO\overset{+}{C}H_2+\overset{+}{C}_2H_5]$
400	100.0	24.6	100.0	14.6	$M-[CH(OSiMe_3)=CH(OSiMe_3)]$
310	10.1	3.2	10.5	1.3	*m/e* 400 $-Me_3SiOH$
205	63.6	27.8	76.6	17.9	$CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
147	10.1	25.4	18.1	27.0	$Me_3Si-O-\overset{+}{S}iMe_2$
117	7.7	13.5	18.1	12.4	
103	2.4	5.7	5.5	6.2	$Me_3SiO\overset{+}{C}H_2$
73	5.7	100.0	11.8	100.0	$Me_3\overset{+}{S}i$

The major fragments resulting from electron-impact ionization of the butaneboronate–trimethylsilyl derivatives of **2–9** (see Scheme 2) are assigned as shown in Tables VII–XI. As expected, the derivatives of compounds possessing pairs of hydroxyl groups able to form perboronate cyclic esters, such as **1**, **2**, and **9**, showed the absence of a trimethylsilyl group [lack of ions at *m/e* 73, 103, M − 90 (or 89), and M − 103], and the molecular ions agreed with those of perbutaneboronates ($M^{\ddagger}$ 346 and $M^{\ddagger}$ 584, respectively). On the other hand, the derivatives of **3**, **4**, **5**, **6**, **7**, and **8** that have a polyhydroxyalkyl chain containing an odd number of hydroxyl groups showed the presence of a trimethylsilyl group [presence of ions at *m/e* 73, 89 (or 90), or 103, or both] in addition to the boronate cycle. Comparison of the structures of the compounds possessing substituent **b** (**3**, **4**, **5**, and **6**) with those of the compounds having substituent **c** (**7** and **8**) showed that the former compounds would predominantly form a 1,2-boronate cycle, leaving free the terminal primary alcohol group, whereas the latter compounds would mainly give a 3,4-boronate cycle involving the terminal primary alcohol group. This observation suggests that the formation of the boronate cycle probably depends on the conformation of each substituent.



Scheme 2. Fragmentation patterns of perbutaneboronate and butaneboronate–trimethylsily derivatives of **2–9**.

TABLE IV

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE TRIMETHYLSILYL ETHERS OF **5** AND **6**

m/e	*Intensity* (%)				*Assignments*
	Me_3Si ether of **5**		*Me_3Si ether of* **6**		
	20 eV	*70 eV*	*20 eV*	*70 eV*	
692	22.5		33.9	7.8	M
677	15.0		14.6	6.6	$M-\overset{+}{C}H_3$
560	4.5		20.8	1.4	$M-Me_3SiO\overset{+}{C}H_2$
488	37.5		85.9	12.8	$M-CH(OSiMe_3)=CH(OSiMe_3)$
398	13.8		4.2	3.9	$M-[CH(OSiMe_3)=CH(OSiMe)+(CH_3)_3SiOH]$
355	7.5		5.2	3.3	
295	27.0		15.6	9.5	$m/e\ 488-Me_3SiO\overset{+}{C}H_2$
283	67.5		5.2	23.9	$m/e\ 488-CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
205	100.0		100.0	36.5	$CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
147	21.3		26.0	26.8	$Me_3Si-O-\overset{+}{S}iMe_2$
117	15.0		20.8	16.6	
103	5.5		9.4	4.3	$Me_3SiO\overset{+}{C}H_2$
73	11.3		15.6	100.0	$Me_3\overset{+}{S}i$

EXPERIMENTAL

Materials. — 5-(D-*arabino*-Tetrahydroxybutyl)-2-methylpyrazine (**1**) and 6-(D-*arabino*-tetrahydroxybutyl)-2-methylpyrazine (**2**) were prepared by the method of Hough *et al.*[4], and 2,5-di-(D-*arabino*-tetrahydroxybutyl)pyrazine (**9**) by that of Fujii *et al.*[22]. 2-(D-*glycero*-2,3-Dihydroxypropyl)-5-(D-*threo*-trihydroxypropyl)pyrazine[12] (**3**), 2-(D-*glycero*-2,3-dihydroxypropyl)-6-(D-*threo*-trihydroxypropyl)pyrazine[12] (**4**), 2,5-di-(D-*threo*-trihydroxypropyl)pyrazine[14] (**5**), 2,6-di-(D-*threo*-trihydroxypropyl)-pyrazine[14] (**6**), 2-(D-*arabino*-tetrahydroxybutyl)-5-(D-*erythro*-2,3,4-trihydroxybutyl)-pyrazine[8] (**7**), and 2-(D-*arabino*-tetrahydroxybutyl)-6-(D-*erythro*-2,3,4-trihydroxy-butyl)pyrazine[8] (**8**) were prepared as previously described.

Pertrimethylsilyl ether of polyhydroxyalkylpyrazines. — These ethers were prepared by a modification of the method of Sweeley *et al.*[23]: each polyhydroxyalkyl-pyrazine compound (10 mg) was dissolved in *N*,*N*-dimethylformamide (0.5 ml) and hexamethyldisilazane (0.2 ml), followed by addition of chlorotrimethylsilane (0.1 ml). The solution was heated for 3 min at 100° in a sealed tube, and then the solution was

TABLE V

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE TRIMETHYLSILYL ETHERS OF **7** AND **8**

m/e	*Intensity* (%)				*Assignments*
	Me_3Si ether of **7**		*Me_3Si ether of* **8**		
	20 eV	*70 eV*	*20 eV*	*70 eV*	
808	30.0	4.4	80.0	4.9	M
793	14.5	3.0	21.5	1.7	$M-\overset{+}{C}H_3$
603	4.5	1.2	8.5	0.7	$M-CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
574	22.9	3.8	70.8	7.3	$M-[CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)+\overset{+}{C}_2H_5]$
502	13.1	2.1	38.5	3.9	$M-CH(OSiMe_3)=C(OSiMe_3)-CH_2(OSiMe_3)$
307	100.0	18.5	100.0	12.7	$CH_2(OSiMe_3)-CH(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
277	7.1		10.8		$m/e\,307-2\overset{+}{C}H_3$
217	56.0	21.0	76.9	17.8	$CH(OSiMe_3)=CH-\overset{+}{C}H(OSiMe_3)$
205	4.8	14.0	11.5	12.7	$CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
189	2.6		4.3		$m/e\,205-CH_4$
147	2.0	23.4	4.6	25.4	$Me_3Si-O-\overset{+}{S}iMe_2$
103	30.4	44.4	50.0	37.6	$Me_3SiO\overset{+}{C}H_2$
73	2.6	100.0	5.4	100.0	$Me_3\overset{+}{S}i$

evaporated *in vacuo* in a desiccator. The residue was dissolved in hexane (0.5 ml) and analyzed by g.l.c. and g.l.c.–m.s.

Butaneboronate–trimethylsilyl derivatives of polyhydroxyalkylpyrazines. — The butaneboronate–trimethylsilyl derivatives of **1–9** were prepared by the method of Wood *et al.*[17]. Each compound (10 mg) was dissolved in anhydrous pyridine (0.5 ml), and butaneboronic acid (12.5 mg) was added to the solution. The solution was heated for 10 min at 100° in a sealed tube. After the reaction mixture had cooled, hexamethyldisilazane (0.4 ml) and chlorotrimethylsilane (0.2 ml) were added. The solvent was evaporated in a desiccator under reduced pressure, and the residue dissolved in a small amount of ether and analyzed by g.l.c. and g.l.c.–m.s.

Gas-liquid chromatography. — G.l.c. was performed with a Shimazu Model GC-6A gas chromatograph equipped with a glass column (0.3 × 100 cm) of 1% Silicone OV-1 on Anachrom SD (100–110 mesh). The oven temperature was programmed to increase at a rate of 6° per min from 140° to 270°. Injection and detector temperatures were held constant at 290°.

Combined gas-liquid chromatography–mass spectrometry. — G.l.c.–m.s. analysis was performed with a Hitachi Model RMU-6MG gas chromatograph–mass spectro-

TABLE VI

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE TRIMETHYLSILYL ETHER OF **9**

m/e	*Intensity* (%)		*Assignments*
	20 eV	*70 eV*	
896	25.1	1.0	M
881	6.0	0.8	$M-\overset{+}{C}H_3$
706	4.0		$M-Me_3SiOH$
662	35.8	1.1	$M-[CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)+\overset{+}{C}_2H_5]$
590	14.2	0.5	$M-CH_2(OSiMe_3)=C(OSiMe_3)-CH_2(OSiMe_3)$
307	100.0	18.3	$CH_2(OSiMe_3)-CH(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
277	10.0		$m/e\ 307-C_2H_6$
217	89.5	22.7	$CH(OSiMe_3)=CH-\overset{+}{C}H(OSiMe_3)$
205	16.3	11.9	$CH_2(OSiMe_3)-\overset{+}{C}H(OSiMe_3)$
147	4.5	22.7	$Me_3Si-O-\overset{+}{S}i(CH_3)_2$
103	69.8	58.7	$Me_3SiO\overset{+}{C}H_2$
73	8.0	100.0	$Me_3\overset{+}{S}i$

meter using an all glass jet separator as the g.l.c.–m.s. interface. The gas chromatographic conditions were the same as those just described. The interface temperature was 300°. The mass spectrometer was operated under the following conditions: ionizing electron energy of 20 or 70 eV, ion accelerating voltage of 3.2 kV (*m/e* max. 1500), total emission of 100 μA, and ion source temperature of 180°.

TABLE VII

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE BUTANEBORONATE–TRIMETHYLSILYL DERIVATIVE OF **2**

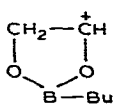
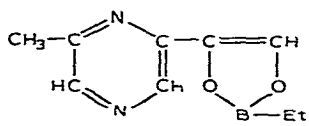
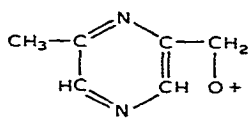
m/e	*Intensity* (%) (*20 eV*)	*Assignments*
346	33.6	M
317	7.1	M − $\overset{+}{C}_2H_5$ (M − 29)
304	16.1	M − C_3H_6 (M − 42)
289	43.6	M − $\overset{+}{C}_4H_9$ (M − 57)
262	34.8	M − $(C_4H_9)BO$ (M − 84)
245	27.4	M − (C_4H_9)—B(OH)—O (M − 101)
219	100.0	M − CH_2—$\overset{+}{C}H$ (M − 127) 
205	33.6	*m/e* 262 − $\overset{+}{C}_4H_9$
190	61.3	*m/e* 219 − $\overset{+}{C}_2H_5$ 
161	27.4	*m/e* 190 − $\overset{+}{C}_2H_5$
123	25.8	 (M − 223)
57	12.3	$\overset{+}{C}_4H_9$

TABLE VIII

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE BUTANEBORONATE–TRIMETHYLSILYL DERIVATIVES OF 3 AND 4

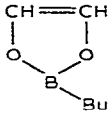
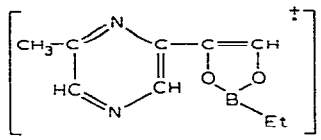
m/e	*Intensity (%) (20 eV)*		*Assignments*
	Deriv. of 3	*Deriv. of* 4	
448	4.1	9.6	M
433	16.3	20.9	M − $\overset{+}{C}H_3$ (M − 15)
391		4.8	M − $\overset{+}{C}_4H_9$ (M − 57)
358	6.0	5.7	M − Me_3SiOH (M − 90)
345	25.1	44.9	M − $Me_3SiO\overset{+}{C}H_2$ (M − 103)
322	100.0	100.0	M −  (M − 126)
232	12.6	49.2	*m/e* 322 − Me_3SiOH
219	38.9	13.8	*m/e* 322 − $Me_3SiO\overset{+}{C}H_2$
207	4.7	13.2	
190	13.3	13.5	*m/e* 219 − $\overset{+}{C}_2H_5$ 
117		13.5	
103	7.9	10.0	$Me_3SiO\overset{+}{C}H_2$
73	13.8	18.7	$Me_3\overset{+}{Si}$
57	8.6	17.0	$\overset{+}{C}_4H_9$

TABLE IX

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE BUTANEBORONATE–TRIMETHYLSILYL DERIVATIVES OF **5** AND **6**

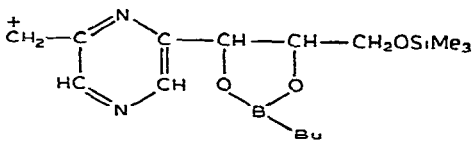
m/e	*Intensity* (%) (*20 eV*)		*Assignments*
	Deriv. of **5**	*Deriv. of* **6**	
536	20.5	43.9	M
521	63.9	56.8	M − $\overset{+}{C}H_3$ (M−15)
494	7.9	16.5	M − C_3H_6 (M−42)
479	7.8	9.5	M − $\overset{+}{C}_4H_9$ (M−57)
446	46.5	26.2	M − Me_3SiOH (M−90)
433	100.0	100.0	M − $Me_3SiO\overset{+}{C}H_2$ (M − 103)
404	20.1	11.0	*m/e* 433 − $\overset{+}{C}_2H_5$
403	11.5	51.9	
343	41.0	40.0	*m/e* 433 − Me_3SiOH
320	38.5	35.0	M − 216 , 
299	23.8	10.3	
199	16.4	10.8	
117	6.0	25.8	
103	78.0	16.9	$Me_3SiO\overset{+}{C}H_2$
73	50.0	26.9	$Me_3\overset{+}{Si}$

TABLE X

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE BUTANEBORONATE–TRIMETHYLSILYL DERIVATIVES OF **7** AND **8**

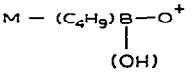
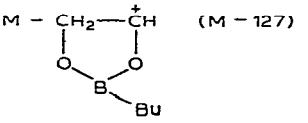
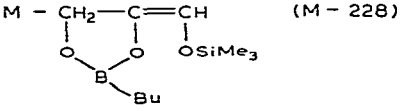
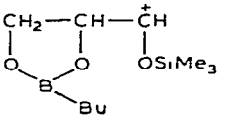
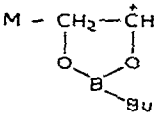
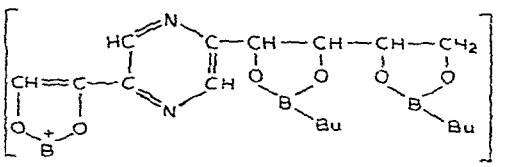
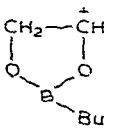
m/e	*Intensity* (%) (*20 eV*)		*Assignments*
	Deriv. of **7**	*Deriv. of* **8**	
574	10.7	20.0	M
559	11.9	13.8	$M - \overset{+}{C}H_3$ (M − 15)
517	5.0	16.2	$M - \overset{+}{C}_4H_9$ (M − 57)
490	16.1	42.0	$M - (C_4H_9)BO$ (M − 84)
475	29.8	32.4	$M - (CH_3)_3SiO^+$ (M − 89)
473	4.0	8.6	
447	66.2	29.0	 (M − 127)
346	100.0	100.0	 (M − 228)
229	21.5	10.0	
149	8.7	17.5	$Me_3SiO\overset{+}{C}H_2$
103	55.2	14.0	
73	20.3	6.0	$Me_3\overset{+}{S}i$

TABLE XI

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF THE BUTANEBORONATE–TRIMETHYLSILYL DERIVATIVE OF 9

m/e	*Intensity* (%) (*20 eV*)	*Assignments*
584	100.0	M
555	17.0	M − $\overset{+}{C}_2H_5$ (M − 29)
542	62.8	M − C_3H_6 (M − 42)
527	65.5	M − $\overset{+}{C}_4H_9$ (M − 59)
500	81.2	M − $(C_4H_9)BO$ (M − 84)
484	28.0	M − $(C_4H_9)BO_2$ (M − 100)
457	80.5	M −  (M − 127)
428	68.4	*m/e* 457 − $\overset{+}{C}_2H_5$
399	30.2	*m/e* 428 − $\overset{+}{C}_2H_5$
361	45.1	
301	23.3	*m/e* 428 − 
273	15.4	
139	27.9	
117	10.0	*m/e* 301 − C_2H_4
57	4.5	$\overset{+}{C}_4H_9$

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