Carbohydrate Research, 74 (1979) 349–353

Note

Preparation and mass-spectrometric analysis of some partially methylated alditol acetates from D-galactose

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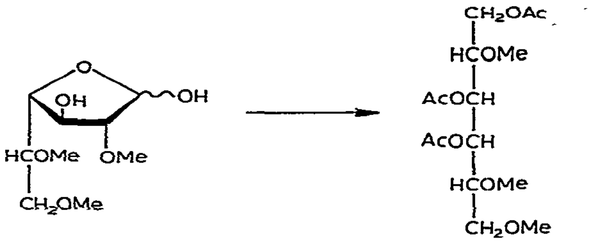
(Received January 16th, 1979; accepted for publication, February 13th, 1979)

In a previous communication[1], primary mass-spectral fragmentation-patterns of the tri-*O*-methylalditol triacetates (**1** and **2**) from 2,5,6-tri-*O*-methyl-D-galactose and 3,5,6-tri-*O*-methyl-D-galactose were reported. Compound **1** also gave very intense, secondary-fragmentation peaks having *m/e* 129 and 143. In order to explain the formation of these fragments, it was necessary to prepare the alditol peracetates (**3**, **4** and **5**) from 5,6-di-*O*-methyl-D-galactose, 4,5,6-tri-*O*-methyl-D-galactose, and 1,4,5,6-tetra-*O*-methyl-D-galactose, respectively. These three compounds, not reported previously, were prepared, and their mass spectra were studied. The g.l.c. and mass-spectral data are presented in Table I.

Primary fragments[2,3] arising by fission of the bond between two carbon atoms in the carbon chain of the alditol were formed as expected. Secondary fragments of interest are the peaks having *m/e* 101, 129, 143, 173, and 175. The fragment having *m/e* 101 was probably formed by elimination of ketene and formaldehyde from the secondary fragment having *m/e* 173. For compound **2**, the fragment having *m/e* 173 was formed from the primary fragment having *m/e* 205 by elimination of methanol, and, in the case of compound **5**, also from the primary fragment having *m/e* 233 by elimination of acetic acid. The peaks having *m/e* 101 and 173 were present for compounds **2** and **5** only. The secondary fragment having *m/e* 143, which is present only for compound **1**, was probably formed by simultaneous elimination of ketene and two acetic acid from the primary fragment having *m/e* 305. The fragment having *m/e* 175 was probably formed from *m/e* 277 by elimination of acetic acid and ketene.

The fragment having *m/e* 129 was formed from all of the compounds (**1** to **5**). For compound **2**, this fragment could have been formed by elimination of acetic acid from the primary fragment having *m/e* 189, but this fragment cannot be formed from the other compounds by the same mechanism. It is evident from the results in Table I that all compounds having the grouping -CHOMe-CHOAc-CHOAc- gave the secondary fragment having *m/e* 129. A cyclic mechanism, **10**–**13**, analogous to the McLafferty elimination, was probably responsible for its formation.



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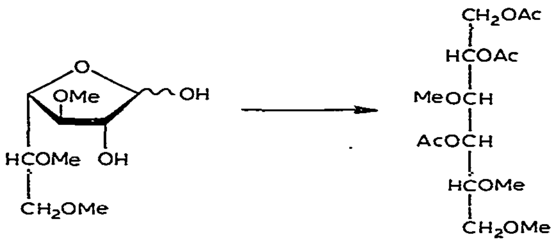

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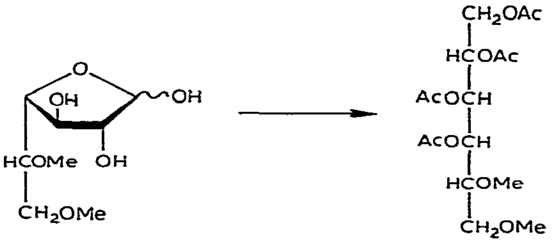

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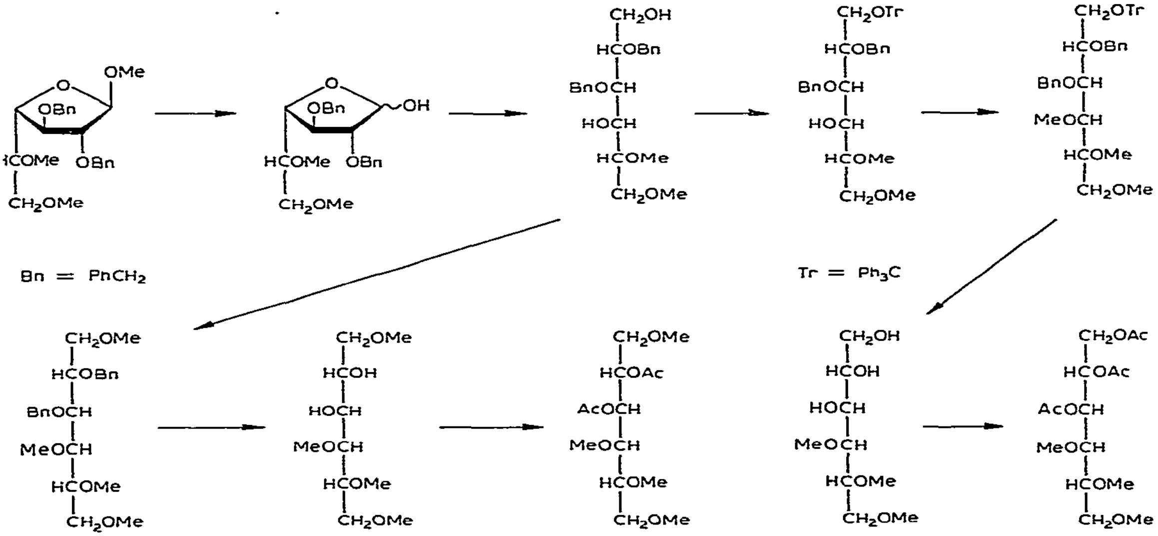


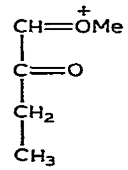
5

4

TABLE I

PERCENTAGES OF DIFFERENT FRAGMENTS IN THE MASS SPECTRA OF ALDITOL ACETATES

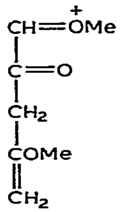
Compound	*Retention time (min)*	m/e (%)																
		43	45	87	89	101	117	129	143	173	175	189	205	233	261	277	305	333
1	2.27	100	30	50	56	0	90	66	75	0	10	0	0	0	0	6	56	0
2	2.21	90	30	50	67	33	0	100	0	10	0	50	20	0	0	0	35	0
3	2.76	100	35	40	90	0	0	62	0	0	0	0	0	0	0	0	0	42
4	1.93	100	80	90	90	0	0	75	0	0	0	0	0	0	20	0	5	0
5	0.83	80	70	55	33	40	0	60	0	33	0	0	0	100	0	0	0	0



$\mathrm{\overset{+}{C}H{=}\overset{+}{O}Me{-}C({=}O){-}CH_2{-}CH_3}$

m/*e* 101

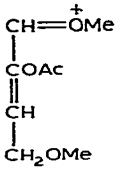
6



$\mathrm{CH{=}\overset{+}{O}Me{-}C({=}O){-}CH_2{-}C(OMe){=}CH_2}$

m/*e* 143

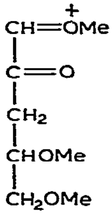
7



$\mathrm{CH{=}\overset{+}{O}Me{-}C(OAc){=}CH{-}CH_2OMe}$

m/*e* 173

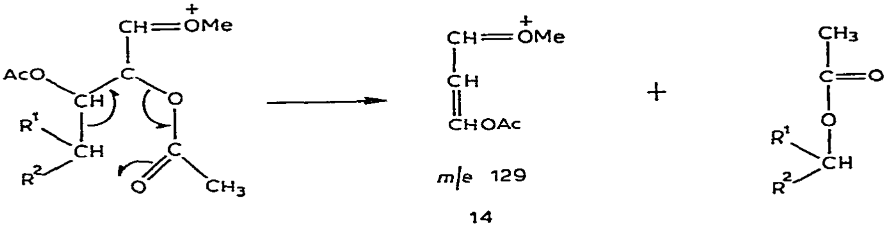
8



$\mathrm{CH{=}\overset{+}{O}Me{-}C({=}O){-}CH_2{-}CHOMe{-}CH_2OMe}$

m/*e* 175

9



10 R^1 = OMe, R^2 = CH_2OAc
11 R^1 = OAc, R^2 = CH_2OAc
12 R^1 = OAc, R^2 = H
13 R^1 = OMe, R^2 = H

EXPERIMENTAL

*1,2,3,4-Tetra-*O*-acetyl-5,6-di-*O*-methyl-*D*-galactitol* (**3**). — This compound was prepared from methyl 5,6-di-*O*-methyl-β-D-galactofuranoside[1] by hydrolysis followed by successive treatment with sodium borohydride and acetic anhydride–pyridine. Compound **3** was isolated as a colorless glass, $[\alpha]_D^{25}$ −18.2° (*c* 1.5, chloroform).

*1,2,3-Tri-*O*-acetyl-4,5,6-tri-*O*-methyl-*D*-galactitol* (**4**). — Methyl 2,3-di-*O*-benzyl-5,6-di-*O*-methyl-β-D-galactofuranoside[1] was hydrolyzed, the sugar reduced with sodium borohydride, the alditol monotritylated, and the trityl ether methylated. The resulting compound was treated with hydrogen in the presence of palladium-on-charcoal, giving the tri-*O*-methyl alditol, which was acetylated to give **4**. This was isolated as a colorless glass, $[\alpha]_D^{25}$ −16.4° (*c* 1.0, chloroform).

Anal. Calc. for $C_{15}H_{24}O_9$: C, 51.72; H, 6.94. Found: C, 52.00; H, 6.70.

*2,3-Di-*O*-acetyl-1,4,5,6-tetra-*O*-methyl-*D*-galactitol* (**5**). — This compound was obtained as for **4**, but omitting the tritylation step; it was isolated as a colorless glass, $[\alpha]_D^{25}$ −11.0° (*c* 1.0, chloroform).

Anal. Calc. for $C_{14}H_{24}O_8$: C, 52.49; H, 7.65. Found: C, 52.23; H, 7.70.

Mass spectra. — The mass spectra were recorded with a Hitachi Mass Spectrometer Model RMU-6L at an ionizing potential of 70 eV.

G.l.c. — A Hewlett–Packard Model 5713A gas chromatograph having a glass column (1.83 m × 6 mm) packed with 3% of ECNSS-M on Gas Chrom Q (100–120 mesh) was used at 160°.

ACKNOWLEDGMENTS

We thank Drs. S. Pakrashi and E. Ali of the Indian Institute of Experimental Medicine, Calcutta, for recording the mass spectra. Our thanks are also due Mr. P. Aich of this Department for technical assistance.

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