Carbohydrate Research, 27 (1973) 471–474

Note

Determination of structure of modified maltose acetates by mass spectrometry*

JERRY GUERRERA AND C EDWIN WEILL

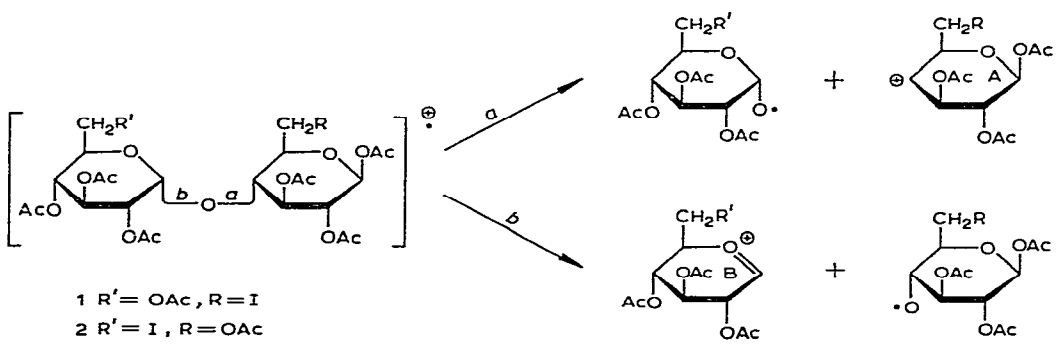
Rutgers University, The State University of New Jersey, Department of Chemistry, Newark, New Jersey, 07102, (U S A)

(Received July 24th, 1972, accepted in revised form January 29th, 1973)

Mass spectrometry has become an important method in the determination of the structure of carbohydrates[1] The mass spectra of monosaccharide acetates permit distinction between ketopyranoses and aldopyranoses, and pyranoses and furanoses[2] The mass spectra of the 6-deoxy-6-halogeno-α-D-glucopyranose tetraacetates have been published[3] Fragmentation patterns of disaccharide derivatives can indicate the type of linkage between the monosaccharide residues[1,4–6] Trisaccharides and tetrasaccharides have been studied as their permethyl ethers[7], trimethylsilyl ethers[6 8] and peracetates[8] The use of 3-methyl-1-naphthyl glycosides has been suggested as an approach for sequential analyses of disaccharides[9]

Under electron-impact ionization, α-D-glucopyranose pentaacetate undergoes loss of the 1-acetoxyl group to yield a peak at *m/e* 331

It seemed likely that selective fragmentation could be used in the sequential analysis of small oligosaccharides in which one or more of the sugar residues has been



1 R'= OAc, R=I
2 R'= I, R=OAc
3 R = OAc, R = H
4 R = H, R = OAc
5 R = OAc, R = OH
6 R = OAc, R = OTs

Chart 1

*Supported by Grant GM-08927 of the National Institute of General Medical Science, National Institutes of Health, U S Public Health Service, and the Rutgers Research Council

chemically modified Such oligosaccharides can be obtained by the action of amylases on amylose molecules in which a portion of the glucose residues has been specifically modified

As the initial interest was in the digests from 6-deoxy-6-iodoamylose and 6-deoxyamylose, the four possible monosubstituted pyranose acetates (**1–4**) thereof were prepared Compounds **1–4**, as well as the precursors **5** and **6**, were subjected to electron-impact mass spectrometry

Chart 1 shows the competing primary fragmentations to be considered Ion "A", resulting from cleavage of bond "*a*", and ion "B" resulting from cleavage of bond "*b*" will have the same *m/e* value only when R′ = R Cleavage of bond "*b*" is favored because carbonium ion "B", which is resonance-stabilized by the free electron pairs on the ring oxygen-atom[2], is more stable than "A" The relative intensities of the "A" and "B" peaks, as compared with the base peak (*m/e* 43), are shown for compounds **1–6** in Table I

TABLE I

RELATIVE INTENSITIES OF MASS-SPECTRAL PEAKS[a]

m/e	*Compound*[b]					
	1	**2**	**3**	**4**	**5**	**6**
331	8 2(B)	2 9(A)	40 2(B)	2 8(A)	8 4(B)	14 5(B)
399	0 36(A)	13 5(B)				
273			5 8(A)	18 1(B)		
289					1 1(A)	
443						1 2(A)

[a]Base peak is *m/e* 43 (100) [b]Letters (A) and (B) refer to carbonium ions (see text)

In all instances the oxonium ion "B" carries a considerable greater proportion of the ion current than ion "A"

The molecular-ion peaks were weak, but could be detected in all spectra The M−·OAc peaks, so useful for identifying the molecular weights of the oligosaccharides, were all present

There are other ions values present that may indicate different fragmentation patterns These include *m/e* 385 for **1**, 317 for **2**, and **4**, 259 for **3**, 275 for **5**, and 429 for **6** Although these values are not especially important in the work for which these experiments were conducted, they are noteworthy The genesis of these ions may be clarified by work in progress with the trideuterioacetates of **1–6**

EXPERIMENTAL

Mass spectra — These were recorded with an AEI MS-902 mass spectrometer at an accelerating potential of 8 kV, and an ionization potential of 70 eV Samples

were introduced via a direct-insertion probe that places the sample almost directly in the ionizing beam The source temperature was 180 ±10°

4-O-(2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl)-1,2,3-tri-O-acetyl-6-deoxy-6-iodo-β-D-glucopyranose (**1**) — The method of Asp and Lindberg[10] was used except that *N,N*-dimethylformamide was employed instead of 2,4-pentanedione as a solvent for the replacement reaction Two recrystallizations from 70% ethanol yielded **1**, m p 131–132°, $[\alpha]_D^{24}$ +54 8° (*c* 1 34, methanol) [lit [10] m p 88–90°, $[\alpha]_D$ +50° on single recrystallization] (Found C, 41 85, H, 4 73, I, 16 88 $C_{26}H_{35}IO_{17}$ calc C, 41 84, H, 4 73, I, 17 00%)

1,2,3,6-Tetra-O-acetyl-4-O-(2,3,4-tri-O-acetyl-6'-deoxy-6'-iodo-α-D-glucopyranosyl)-β-D-glucopyranose (**2**) — 2,3,2',3',4'-Penta-*O*-acetyl-1,6-anhydro-6'-deoxy-6'-iodo-β-maltose[11] (100 mg) was dissolved in 2 ml of a 1 70 30 sulfuric acid–acetic anhydride–acetic acid solution, which was kept for 3 5 h at room temperature The flask was cooled to 0°, 5 ml of water was added, and the acid was neutralized with saturated $NaHCO_3$ solution After centrifugation, the precipitate was washed with 3 × 3 ml of water, with centrifugation after each washing The precipitate was dissolved in ethanol and evaporated under a stream of nitrogen Two recrystallizations from ethyl acetate–hexane yielded 60 mg of **2**, m p 86–87°, $[\alpha]_D^{24}$ +82 4° (*c* 0 73, methanol) (Found C, 42 06, H, 4 78, I, 16 41 $C_{26}H_{35}IO_{17}$ calc C, 41 84, H, 4 73, I, 17 00%)

4-O-(2 3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl)-1,2,3-tri-O-acetyl-6-deoxy-β-D-glucopyranose (**3**) — Compound **1** (300 mg) was dissolved in 10 ml of ethanol, to which was added 0 1 ml pyridine and 300 mg of 10% palladium on charcoal The flask was heated to 65°, and hydrogen was bubbled through the solution for 5 h The contents were centrifuged, and the supernatant liquid removed The catalyst was washed with 5 ml of ethanol, centrifuged, and the supernatant liquid added to the first liquid The combined supernatants were filtered and evaporated under nitrogen The gummy residue was dissolved in 10 ml of chloroform, washed with 5 ml of sodium thiosulfate (1%), and 4 × 10 ml of water, dried over calcium chloride, and the chloroform removed The residue was dissolved in ethyl acetate (1 ml), and chromatographed through a column (0 5 cm × 7 cm) of charcoal–Celite (50 50, w w), with ethyl acetate as eluant Tubes 3 and 4 of 12 fractions yielded crystalline **3** on evaporation, m p 160–161°, $[\alpha]_D^{24}$ +70 5° (*c* 1 10, chloroform) (Found C, 49 99, H, 5 98 $C_{26}H_{36}O_{17}$ calc C, 50 32, H, 5 80%)

1,2,3,6,2',3',4'-Hepta-O-acetyl-6'-deoxy-β-maltose (**4**) — This compound was prepared from 2,3,2',3',4'-penta-*O*-acetyl-1,6-anhydro-6'-deoxy-β-maltose[11] by the same method used in the preparation **2** except that the product was crystallized from ethanol, m p 184–186° (lit [11] 183–185°)

1,2,3,2',3',4',6'-Hepta-O-acetyl-β-maltose (**5**) and *1,2,3,2',3',4',6'-hepta-O-acetyl-6-O-p-tolylsulfonyl-β-maltose* (**6**) were prepared according to Asp and Lindberg[10]

REFERENCES

1 For a review, see N K KOCHETKOV AND O S CHIZHOV, *Advan Carbohyd Chem*, 21 (1966) 39
2 K BIEMANN, D C DEJONGH, AND H K SCHNOES, *J Amer Chem Soc*, 85 (1965) 1763
3 O S CHIZHOV, A B FOSTER, M JARMAN, AND J H WESTWOOD, *Carbohyd Res*, 22 (1972) 37
4 N K KOCHETKOV, O S CHIZHOV AND L A POLIAKOVA, *Dokl Akad Nauk SSSR*, 158 (1964) 685
5 O S CHIZHOV, N V MOLODTSOV, AND N K KOCHETKOV, *Carbohyd Res*, 4 (1967) 273
6 N K KOCHETKOV, O S CHIZHOV, AND N V MOLODTSOV, *Tetrahedron*, 24 (1968) 5587
7 J KARKKAINEN, *Carbohyd Res*, 17 (1971) 1
8 W W BINKLEY, R C DOUGHERTY, D HORTON, AND J D WANDER, *Carbohyd Res*, 17 (1971) 127
9 J KARLINER, *Tetrahedron Lett*, 32 (1968) 3545
10 L ASP AND B LINDBERG, *Acta Chem Scand*, 6 (1952) 941
11 G G S DUTTON AND K N SLESSOR, *Can J Chem*, 44 (1966) 1069