#### Note

# Internal glycosides present in hydrolyzates of *O*-(2-hydroxyethyl)starch: Spectroscopic characterization of 3,4,6-tri-*O*-acetyl-1,2-*O*-ethylene- $\beta$ -D-glucopyranose and 3,5,6-tri-*O*-acetyl-1,2-*O*-ethylene- $\alpha$ -D-glucofuranose

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This report describes the characterization of 3,4,6-tri-O-acetyl-1,2-O-ethylene- $\beta$ -D-glucopyranose (1) and 3,5,6-tri-O-acetyl-1,2-O-ethylene- $\alpha$ -D-glucofuranose (2) by spectroscopic methods The elucidation of these structures confirms the earlier identification of two nonreducing products isolated from acid hydrolyzates of O-(2-hydroxy-ethyl)starch as the nonacetylated analogues (3 and 4) of 1 and 2, respectively<sup>1-7</sup>

Earlier workers had reported the preparation of the  $\beta$ -D pyranose<sup>8</sup> 3 and its  $\alpha$ -D anomer<sup>9</sup> (5) by the internal Williamson reaction of the anomeric 2-haloethyl 2,3,4,6-tetra-O-acetyl-D-glucopyranosides, the anomeric configurations of the gluco-side precursors were assigned on the basis of optical rotational data<sup>8</sup>, and retention of the stereochemistry at C-1 in the reaction was assumed The  $\alpha$ -D furanose isomer (4) was prepared<sup>6</sup> in a similar manner and found to exhibit optical rotatory behavior



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similar to that of methyl  $\alpha$ -D-glucofuranoside; it was further observed that the p m r spectrum of compound 4 in deuterium oxide exhibits a narrow doublet for the H-1 signal, and on this basis the  $\alpha$ -configuration was assigned to this cyclic ether<sup>6a</sup>

Partial mass spectra of 3,4,6-tri-O-acetyl-1,2-O-ethylene- $\alpha$ -D-glucopyranose<sup>8</sup> and 3,5,6-tri-O-acetyl-1,2-O-ethylene- $\alpha$ -D-glucofuranose<sup>9</sup> (2) are recorded in Table I, together with tentative identifications of the fragment ions Decomposition of the pyranose derivative 1 leads to the formation of the acetyl (m/e 43) and acetoxymethyl (m/e 73) cations as essentially the only positively charged fragments, whereas bond

TABLE I

m/e	Intensity in	n spectrum of	Assignment		
	2	1			
332	0 005	0 004	M‡		
331	0 01	• • • •	M <sup>+</sup> -H		
289	0 05		M <sup>+</sup> -Ac		
273	0 13	0 02	M <sup>+</sup> - OAc		
272	0 36	0 033	$M^{+}$ -AcOH or -2CH <sub>2</sub> O		
259	0 12		$M^+ - CH_2OAc$		
230	0 35	0 11	$M^+ - Ac_2O$		
229	9 16		$M^{+}-Ac - AcOH $ or $-Ac - 2CH_2O$		
213	16	0 04	$273 - AcOH \text{ or } -2CH_2O$		
212	17 3	0 12	$M^+$ -2AcOH or -AcOH-2CH <sub>2</sub> O		
199	0 14	0 17	$259 - AcOH \text{ or } -2CH_2O$		
187	94		M <sup>+</sup> -AcOCH <sub>2</sub> CHOAc		
170	20 4	04	$230 - AcOH \text{ or } -2CH_2O$		
158	21	0 04	[AcOCHCHCH <sub>2</sub> OAc] <sup>+</sup>		
157	42	03	AcOCHCH=CHOAc		
153	34	01	$M^{\ddagger} - OAc - AcOH - 2CH_2O \text{ or } M^+ - OAc - 2AcOH$		
145	49	01	AcOCHCH2OAc. Ac30+		
144	66	01	[AcOCHCHOAc] <sup>+</sup>		
139	09	02	acetoxypyrilum		
127	44 6		$187 - AcOH \text{ or } -2CH_2O$		
116	12 5	01	-		
115	12 6	03			
110	0 95	01	$M^+ - Ac_2O - AcOH - 2CH_2O$		
103	24	01	$145 - CH_2CO, Ac_2OH^+$		
102	50	02			
99	9.4	02			
98	43	01			
97	18	0.2	hydroxypynlium		
87	11 2	03			
86	11 8	12			
81	24	05	pyrilium		
73	34 5	35 0	AcOCH <sub>2</sub> +		
43	100	100	Ac <sup>+</sup>		

INTENSITIES<sup>4</sup> OF MAJOR IONS OBSERVED FROM MASS SPECTRAL DECOMPOSITION OF 1 AND OF 2

"Expressed as per cent of the base peak

ruptures in the furanose derivative 2 lead to a number of other, significantly contributing fragments Most notable among these are m/e 187, which is characteristic<sup>10</sup> of scission of the C-4–C-5 bond of aldohexofuranose acetates, and m/e 127, which is derived from the preceding ion by loss of either the elements of acetic acid or the 1,2-O-ethylene group (presumably as two molecules of formaldehyde) The mass equivalence of these two  $C_2H_4O_2$  fragments (–OCH<sub>2</sub>CH<sub>2</sub>O– and CH<sub>3</sub>CO<sub>2</sub>H) renders the interpretation of the fragmentation pathways ambiguous, sufficient information, however, is available that specific deuteration techniques<sup>11</sup> are not necessary to clarify the assignment The foregoing mass-spectral data verify that compound 2 is indeed a furanose derivative, whereas the isomer 1 appears to possess the anticipated, six-membered ring structure, the latter conclusion arises from the observation<sup>12</sup> that tetrahydrofurylium cations far exceed the corresponding tetrahydropyrilium ions in stability Similar conclusions can be drawn from the mass spectra<sup>13</sup> of the parent compounds 3 and 4, in which m/e 175 (M<sup>+</sup> – CH<sub>2</sub>OH) and m/e 145 (M<sup>+</sup> – CHOH-CH<sub>2</sub>OH), respectively, are observed as major fragments

Cursory comparison of the low-field portion of the 100-MHz p m r spectrum of the  $\beta$ -pyranose triacetate 1 in chloroform-*d*, with that of the methyl 2,3,4,6-tetra-*O*-acetyl- $\alpha$ - and  $\beta$ -D-glucopyranosides<sup>14</sup> (6 and 7, respectively) reveals that, whereas the traces of compounds 1 and 6 are totally dissimilar, the signals of the carbohydrate backbones of 1 and 7 exhibit gross similarity In view of the consideration that these spectra are not readily interpretable but that a substantial body of earlier evidence leads<sup>1-7</sup> to the same conclusion, the  $\beta$ -pyranose form of 1 may be taken confidently as correct

The 100-MHz p m r spectra of compound 2 and 3,5,6-tri-O-acetyl-1,2-O-isopropylidene- $\alpha$ -D-glucofuranose<sup>15</sup> (8) in chloroform-d exhibit a broadly similar, complex relationship of the type just described, in this example, however, redetermination of the spectra of these compounds, with benzene- $d_6$  as the solvent, permits extraction of first-order chemical-shift and spin coupling parameters (Table II) for

## TABLE II

COMPARATIVE N M R SPECTRAL DATA FOR 3,5,6-TRI-O-ACETYL-1,2-O-ETHYLENE-
α-D-GLUCOFURANOSE (2) AND 3,5,6-TRI-O-ACETYL-1,2-O-ISOPROPYLIDENE-α-D-
glucofuranose (8) in benzene- $d_6$

Compound	Chemical shifts (7)										
	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	-CH <sub>2</sub> CH <sub>2</sub> -	OAc	CMe <sub>2</sub>	
2	4 72	6 58	4 52	5 28	4 65	5 19	5 84	6 787 12 6 066 45	8 30, 8 33, 8 37		
8	4 29	5 87	4 45	5 49	4 56	5 28	5 89		8 28, 8 31, 8 34	8 79, 8 88	
	First-order coupling constants (Hz)										
2	$J_{1 \ 2} \\ 2 \ 3$	$J_{2\ 3}$ 15	$J_{3 \ 4} \\ 3 \ 4$	J <sub>45</sub> 99	J <sub>56</sub> 23	J <sub>56</sub> 56	J <sub>6 6</sub> 12 0				
8	34 ·	<0 4	29	95	23	6.1	12 2				

the protons on the carbohydrate skeleton The uniform correspondence of the coupling constants of analogous protons indicates extreme conformational similarity in the sugar portions of these two molecules As such an observation simply cannot be reconciled with a *trans*-fused structure for compound 2, the anomeric configuration of this furanose derivative is unquestionably  $\alpha$ , which confirms the earlier assignment<sup>6</sup> of this stereochemistry to the unacetylated furanose form 4

#### EXPERIMENTAL

3,4,6-Tri-O-acetyl-1,2-O-ethylene- $\beta$ -D-glucopyranose<sup>8</sup> (1) had m p 121-122°,  $[\alpha]_D + 52^\circ$  (c 1 0, chloroform), acetylation of 1,2-O-ethylene- $\alpha$ -D-glucofuranose with acetic anhydride and pyridine gave the crystalline triacetate (2), m p 95-96°,  $[\alpha]_D 0^\circ$ (c 1 0, chloroform) N m r spectra were recorded at ambient temperature on a conventional Varian HA-100 spectrometer and are referenced to internal tetramethylsilane Mass spectra were determined by Mr C R Weisenberger using an AEI MS-902 high-resolution, double-focusing mass spectrometer at an inlet temperature of 250°, an ionizing potential of 70 eV, and an accelerating potential of 8 kV

### ACKNOWLEDGMENT

The US Department of Agriculture is thanked for support (to HCS.)

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