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THE FORMATION OF α,β-UNSATURATED ALDEHYDES IN THE HYDROLYSIS OF ACETYLATED GLYCALS*†

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ABSTRACT

The hydrolysis of D-glucal triacetate (**1**), D-galactal triacetate (**11**), and D-arabinal diacetate (**6**) in refluxing, aqueous 1,4-dioxane has been investigated; each of these compounds is readily converted into a partially acetylated *aldehydo*-hex-2-enopyranose *via* the related pseudo-glycal. The latter constitutes the major component after brief reaction, and the conversion of each into the unsaturated aldehyde is inhibited in the presence of hydroquinone. Generally, the process is promoted by the addition of some acetic acid. Acetyl migration occurs during the reaction, and isolation of the aldehyde is best effected by acetylating the crude product and fractionating it on dimethyl sulfoxide-impregnated paper. Of the three examples studied, the yield of aldehyde is highest for **1** and lowest for **11**.

INTRODUCTION

In a recent report from this laboratory[1], the formation of 4,5,6-tri-*O*-acetyl-*trans*-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (**3**) in the hydrolysis of tri-*O*-acetyl-D-glucal (**1**) was described, and it was suggested that it may have been the compound that led Emil Fischer to conclude that reduction of "acetobromoglucose" with zinc had produced an aldehyde—hence, his choice of the name acetoglucal[2].

Our initial interest arose from our observation[3] that hydrolysis in neutral media of glycopyranosides bearing fused cyclopropyl rings at C-2, C-3 gives derivatives of aldehydo sugars, the isomeric hemiacetals being completely absent. It was considered that this result might have been due to strain that favored the aldehydo over the lactol form. We were therefore prompted to study ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**17**), as the strain-free hydrolysis product, **2**, was expected to be more stable than the related δ-hydroxy aldehyde **3**. Furthermore the hemiacetal, **2**, would be readily identifiable, as it is the well known di-*O*-acetyl-

†Dedicated to the memory of Dr. Hewitt G. Fletcher, Jr.
*For a preliminary account of this work, see ref. 1.
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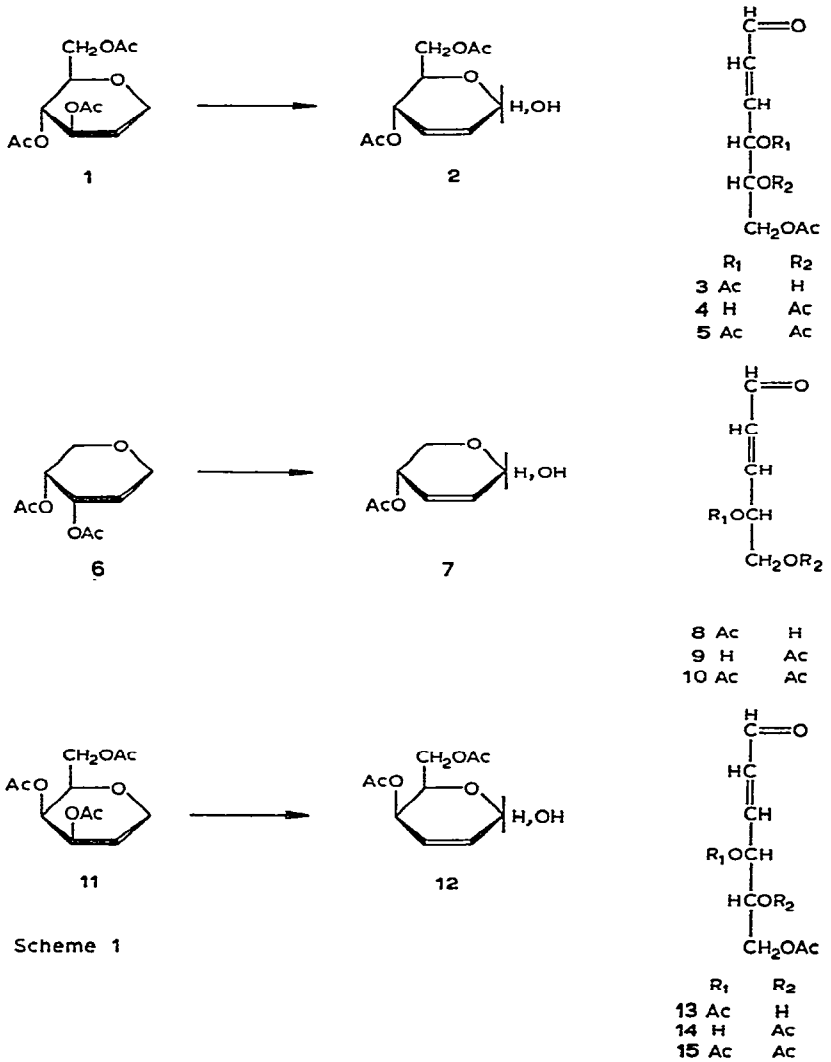
2,3-dideoxy-D-*erythro*-hex-2-enopyranose (pseudo-D-glucal diacetate) formed from **1** n boiling water[4].



Scheme 1

In this paper we report more fully on our earlier observations, and on the extension of our studies to di-*O*-acetyl-D-arabinal (**6**) and tri-*O*-acetyl-D-galactal (**11**).

RESULTS

A solution of the alkene **17** in aqueous 1,4-dioxane was boiled under reflux, and the product was periodically isolated, and examined by proton magnetic resonance

TABLE I

HYDROLYSIS[a] OF TRI-*O*-ACETYL-D-GLUCAL (1)

Conditions		*Time (h)*						
		0.25	*1*	*1.5*	*2*	*3*	*4*	
(i) 1 mmole of 1 in 5 ml of water (pH ~7)	Ratio of 3:2	0.5	2.6	3.5	4.3	4	4.8	
	Conversion (%)	56	60	70	51	45	44	
	3 in mixture (%)	18.7	43.3	54.4	44	36	36.4	
		Time (h)						
		0.25	*1*	*3*	*5*	*7*	*9*	*10.5*
(ii) 1 mmole of 1 in 5 ml of water plus 2 ml of 1,4-dioxane	Ratio of 3:2	0	0.1	0.7	1.2	2.1	3	3.1
	Conversion (%)	22	52	59	50	74	70	53
	3 in mixture (%)	0	4.7	24.3	27.2	50.1	50.2	40.1
		Time (h)						
		0.75	*1.5*	*2.25*	*2.5*	*3.25*	*4.5*	*5.25*
(iii) 1 mmole of 1 in 5 ml of aqueous acetic (A)[b] plus 1 ml of 1,4-dioxane	Ratio of 3:2	0.4	0.5	1	1.1	1.2	2.0	1.4
	Conversion (%)	63	63	73	80	84	80	50
	3 in mixture (%)	18	21	36.5	41.8	45.8	53.3	29.2
		Time (h)						
		1	*1.5*	*2.25*	*2.5*			
(iv) 1 mmole of 1 in 5 ml of aqueous acetic acid (B)[c] plus 1 ml of 1,4-dioxane	Ratio of 3:2	1.4	2.0	2.5	2.0			
	Conversion (%)	80	86	82	76			
	3 in mixture (%)	46.7	57.3	58.6	50.7			

[a]The solutions were boiled under reflux. For determination of reaction progress, see Experimental. [b]The solution (A) contained 1.3 ml of glacial acetic acid in 100 ml of water. [c]The solution (B) contained 2.6 ml of glacial acetic acid in 100 ml of water.

(p.m.r.) spectroscopy. After 14 h, the absorptions due to the ethoxyl aglycon had disappeared, and the presence of **2** was confirmed by its reconversion into **17** by the published procedure[5]. The presence of aldehyde **3** was apparent from a signal at τ 0.38, and it was determined that, after a total reaction-period of 24 h, an optimal situation existed in which the ratio of the aldehyde **3** to the pseudoglucal **2** was 3:2, and together they comprised 68 percent of the reaction mixture (judging from the p.m.r. spectrum).

We re-examined the hydrolysis of tri-*O*-acetyl-D-glucal (**1**) and found that **3** was formed much faster than from **17**. It was presumed that the acetic acid liberated catalyzed the process, and so a number of experiments designed to test this postulate were undertaken. The results, tabulated in Table I and plotted in Fig. 1, indicated the catalytic effect of the added acid.

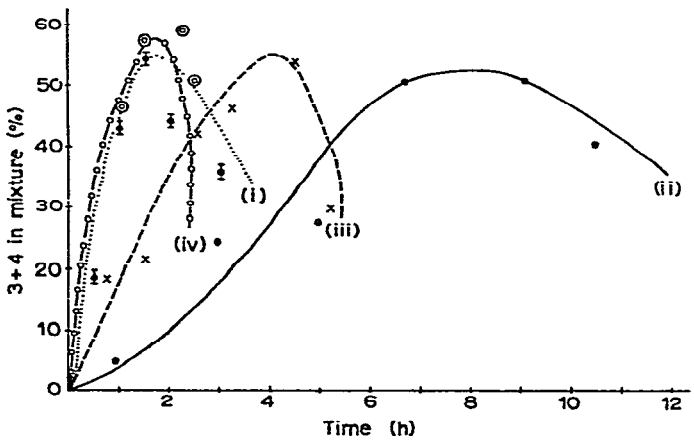


Fig. 1. Formation of *trans*-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose diacetates **3** and **4** in hydrolyses of tri-*O*-acetyl-D-glucal (**1**) (in conjunction with Table I).

The hydrolysis of di-*O*-acetyl-D-arabinal (**6**) was found to follow a similar pattern (see Scheme 1, Table II, and Fig. 2). However, the aldehydic proton at $\tau \sim 0.38$ in the crude hydrolysis product was a complex signal, suggesting a mixture of aldehydes. Indeed, thin-layer chromatography (t.l.c.) revealed the presence of two poorly-resolved components (**8** and **9**), which became one (**10**) upon acetylation. The monoacetates **8** and **9** could not be cleanly separated by column or preparative-layer chromatography, but it was possible to obtain fractions that were enriched in one isomer or the other. Data from the p.m.r. spectra of these fractions were obtained by double-irradiation experiments, and are shown in Table IV. Notably, the parameters for H-4 provided support for the structural assignments as the aldehydes **8** and **9**.

The hydrolysis of tri-*O*-acetyl-D-galactal (**11**) followed a similar course (see Scheme 1) provided that acid was not added. Thus, in aqueous 1,4-dioxane (see Table III and Fig. 3), optimal formation of aldehyde had occurred after 6 h, the ratio

TABLE II

HYDROLYSIS[a] OF DI-*O*-ACETYL-D-ARABINAL (6)

Conditions		*Time (h)*					
		0.25	*1.25*	*2*	*3*	*4*	*7*
(i) 1 mmole of 6 in 5 ml of water plus 2 ml of 1,4-dioxane	Ratio (8+9):7	0.1	1.4	2.0	2.2	2.1	4.1
	Conversion (%)	23	75	84	85	76	60
	(8+9) in mixture (%)	2.3	43.7	56.0	58.5	51.5	48.2
		Time (h)					
		0.25	*0.8*	*1.0*	*1.25*	*1.6*	
(ii) 1 mmole of 6 in 5 ml of aqueous acetic acid (A)[b] plus 2 ml of 1,4-dioxane	Ratio (8+9):7	0.5	1.0	1.2	1.2	1.2	
	Conversion (%)	53	78	80	58	50	
	(8+9) in mixture (%)	17.8	39	43.6	31.6	27.3	
		Time (h)					
		0.5	*1*	*1.25*	*2*	*3*	
(iii) 1 mmole of 6 in 5 ml of aqueous acetic acid (B)[c] plus 2 ml of 1,4-dioxane	Ratio (8+9):7	1.5	1.8	1.9	1.8	3.0	
	Conversion (%)	70	71	60	63	63	
	(8+9) in mixture (%)	42.0	45.6	39.3	40.5	46.1	

[a]For key, see footnotes to Table I.

TABLE III

HYDROLYSIS[a] OF TRI-*O*-ACETYL-D-GALACTAL (**11**)

Conditions		*Time (h)*									
		0.25	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1 mmole of **11** in 5 ml of water plus 2 ml of 1,4-dioxane	Ratio of (**13**+**14**):**12**	0	0	0.2	0.8	1.2	1.3	1.7	2	3	3
	Conversion (%)	0	7.5	14	21	38	31	46	31	30	27
	(**13**+**14**) in mixture (%)	0	0	2.3	9.3	20.7	17.5	29	20.7	22.5	20.3

[a]For key, see footnotes to Table I.

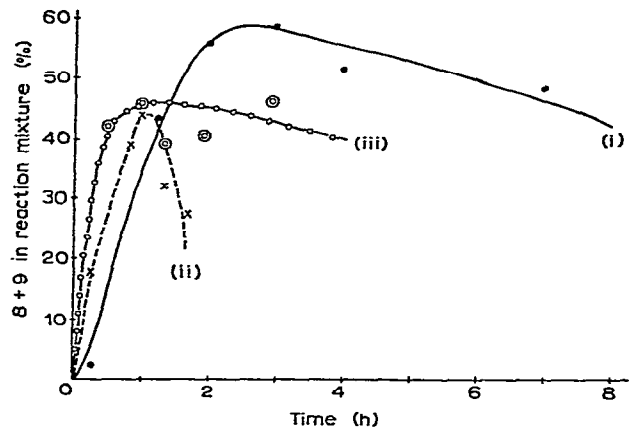


Fig. 2. Formation of *trans*-2,3-dideoxy-*aldehydo*-D-*glycero*-pent-2-enose diacetates **8** and **9** in hydrolyses of di-*O*-acetyl-D-arabinal (**6**) (in conjunction with Table II).

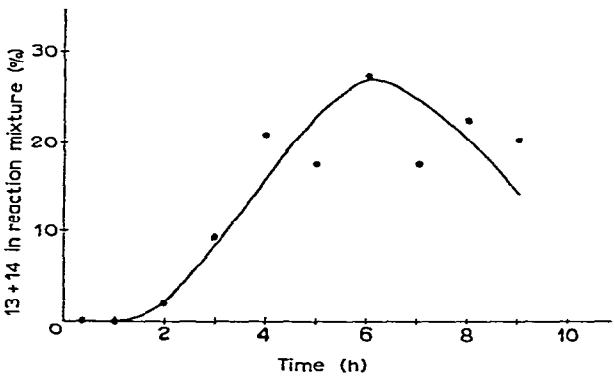


Fig. 3. Formation of *trans*-2,3-dideoxy-*aldehydo*-D-*threo*-hex-2-enose diacetates **13** and **14** in hydrolyses of tri-*O*-acetyl-D-galactal (**11**) (in conjunction with Table III).

of the aldehydes (**13** and **14**) to the pseudogalactal **12** was 1.7:1, and these together comprised 46 percent of the spectrum. However, in acidified solutions, the formation of aldehydes (**13** and **14**) was suppressed.

The complexity of the signal at $\tau \sim 0.38$ again suggested that the product was a mixture of the aldehydes **13** and **14**, but chromatographic separation of these could not be achieved. Furthermore, even isolation of the triacetate **15** was only partially successful. However, on the basis of the experience gained with **8**, **9**, and **10**, it was possible to make the p.m.r. assignments shown in Table IV.

In the light of the formation of the aldehydes (**8** and **9**, and **13** and **14**), the crude hydrolysis product from tri-*O*-acetyl-D-glucal (**1**) was re-examined. Although the aldehydic proton at $\tau \sim 0.38$ appeared to be a clean doublet, evidence for the presence

TABLE IV

SPECTROSCOPIC DATA FOR α,β-UNSATURATED ALDEHYDES

Compounds	*P.m.r. data*[a]						
	Chemical shifts (τ)						
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6(H-5')*	*H-6'*
3	0.38	3.78	3.07	4.43	5.5–6.0		
4	0.38	3.63	3.14	5.40	4.90	5.6–6.0	
5	0.43	3.81	3.30	4.30	4.82	5.75	5.81
8	0.38	3.73	3.13	4.40	6.0–6.3		—
9	0.38	3.58	3.13	5.30	5.5–6.0		—
10	0.36	3.75	3.14	4.23	5.57	5.83	—
13	0.38	3.78	3.08	4.40	5.6–6.0		
14	0.38	3.63	3.10	5.40	4.80	5.8–6.0	
15	0.34	3.77	3.20	4.20	4.60	5.65–6.05	

[a]All p.m.r. spectra were recorded at 60 MHz in $CDCl_3$ (Me_4Si), except that for compound **5**, which w recorded at 220 MHz. The assignments were substantiated by double-irradiation experiments. [b]Unresolv multiplets, u.

of two aldehydes, **3** and **4**, was provided by the p.m.r. spectrum. Thus, H-4 resonated at τ 4.43 for **3**, and at τ 5.40 for **4**, in keeping with related data in Table IV. However, it was not found possible to separate these isomers.

DISCUSSION

Acid-catalyzed additions to glycal double bonds, and allylic rearrangements of acetylated glycals[6], are well established procedures, constituting the preferred routes to 2-deoxyaldoses[7] and pseudoglycals[8], respectively. Our interest during these investigations has, therefore, been focused on the α,β-unsaturated aldehydes, none of which had been obtained prior to our preliminary[1] communication*. However, in the

*Di-*O*-acetyl-pseudo-D-glucal (**2**) and mono-*O*-acetyl-pseudo-D-arabinal (**7**) have occasionally been represented as α,β-unsaturated aldehydes[5,9,11]. However they were not characterized as such, and, although the configurations of the double bonds were not specified, it is clear from the texts that the *cis* isomers were intended. These would certainly exist as hemiacetals.

Coupling constants (Hz)[b]								*U.v.* λ_{max} *(nm)*	*I.r.* ν (cm^{-1})
$J_{1,2}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6}$		
7.2	15.5	1.5	5.0	u	u	u	u		3600, 3300,
7.2	15.5	1.5	5.0	u	u	u	u	217	1735, 1695
7.2	15.5	1.5	5.0	5.0	4.0	5.3	11.5		1735, 1695
7.2	16.0	1.5	4.0	u	u	—	u		3600, 3300,
7.2	16.0	1.5	4.0	u	u	—	u	217	1735, 1695
7.2	15.5	1.5	4.5	4.0	$J_{4,5'}$ 6.0	—	$J_{5,5'}$ 11.5		1735, 1695
7.2	15.5	~1.0	4.5	u	u	u	u		3600, 3300,
7.2	15.5	~1.0	4.5	u	u	u	u	217	1735, 1695
7.2	15.5	~1.0	4.5	4.0	u	u	u		1735, 1695

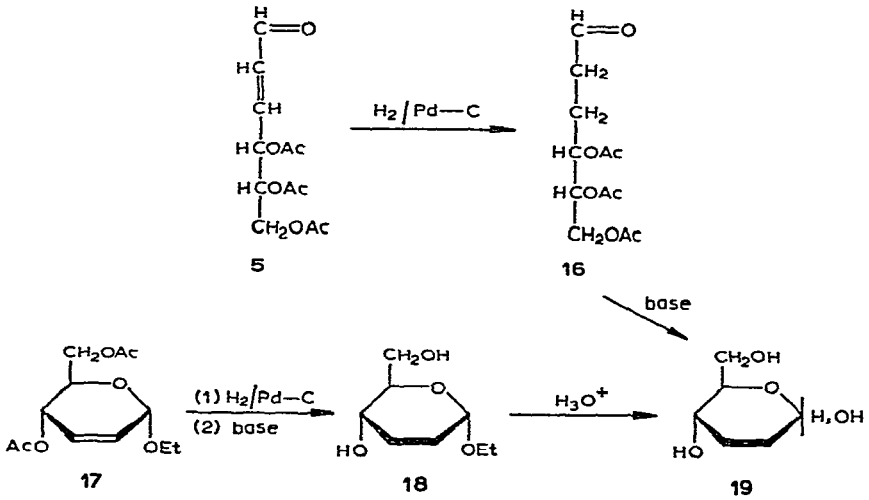
interim, there have been three relevant reports. The first described the formation of **3** by methoxymercuration of tri-*O*-acetyl-D-glucal[12]; the second, the formation of unsaturated aldehydes in hydrolytic reactions of 2-deoxyaldoses[13]; and the third, the preparation of **5** from 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose in two steps[14].

In general, isolation of the aldehydes was best accomplished by acetylating the crude products and fractionating the resulting mixtures on dimethyl sulfoxide-impregnated paper[15]. Isolation was facilitated by viewing the dried paper-chromatograms under ultraviolet light, whereupon the unsaturated aldehyde was visibilized as a strongly absorbing band. Of the aldehydes, separation was most facile for **5**; hence, structural studies were performed on this compound, and the results were used to form a basis for identification of the congeners, **10** and **15**.

The most definitive data for the unsaturated aldehydes (**5**, **10**, and **15**) come from i.r. and u.v. absorption spectra, as, unlike mass spectra, the absorption spectra provide a clear basis for distinguishing between these aldehydes and their pseudo-

glycal isomers (**2**, **7**, and **12**, respectively). Thus, the chromophore in **5**, **10**, and **15** absorbs in the ultraviolet spectrum at 217 nm, and in the infrared spectrum at 1695 and 1735 cm^{-1}. Evidence for the *trans* geometry of the double bond was obtained from the large H-2,H-3 coupling ($J_{2,3}$ ~15.5 Hz) found for all of these aldehydes (see Table IV).

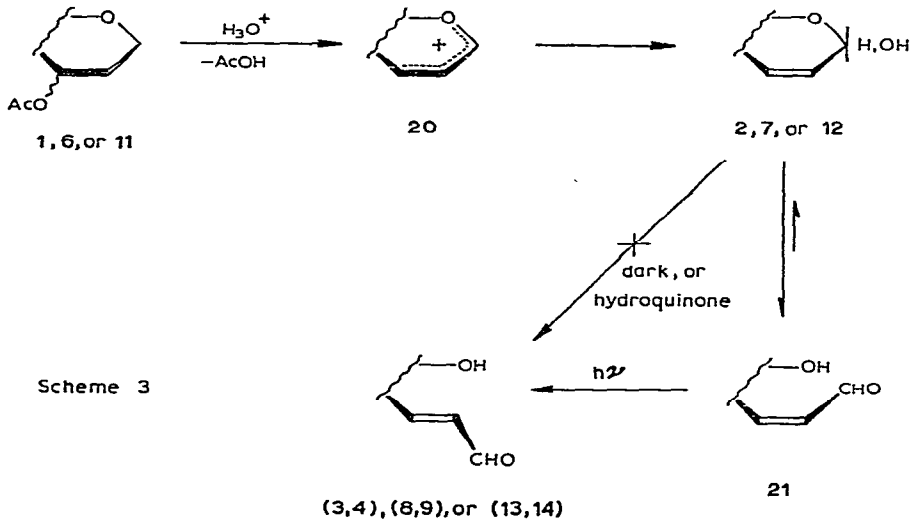
The foregoing assignments based on spectral parameters were validated by chemical methods applied to **5**, the most readily accessible of the aldehydes examined. Both **5** and its dihydro derivative **16** gave (2,4-dinitrophenyl)hydrazones having elemental analyses agreeing with the calculated values. Deacetylation of **16** gave the dideoxyhexose **19**. The latter was alternatively prepared from the alkene **17** *via* the known compound[15] **18** (see Scheme 2).



Scheme 2

The conversion of the pseudoglycals **2**, **7**, and **12** into the unsaturated aldehydes could be conveniently monitored by p.m.r. spectroscopy (see Table IV), by integrating the signals for H-2 and H-3 of the former, and H-1 of the latter. The results (given in Tables I, II, and III, and plotted in Figs. 1, 2, and 3, respectively) indicate clearly that the aldehydes are formed at the expense of the pseudoglycals. There is an optimal reaction-time at which the concentration of aldehyde is highest, and beyond which, decomposition sets in.

The entire process is clearly accelerated by the presence of acid in the reaction medium. In the light of Ferrier's studies[16–18], the formation of the allyl-oxocarbonium ion **20** may be assumed to be the first step (see Scheme 3). The conversion of the pseudoglycals into the unsaturated aldehydes is best rationalized by the intermediacy of the *cis* aldehydes (e.g., **21**), small concentrations of which would be expected to exist in equilibrium with the pseudoglycals. Evidence supportive of this



Scheme 3

rationalization comes from the observation that the formation of **3** was drastically lessened when the hydrolysis was conducted in the dark, and completely inhibited when hydroquinone (0.1 mol. equiv.) was present in the solution. Clearly, these conditions preclude the *cis*→*trans* isomerization of the double bond; compound **21** therefore re-closes to the pseudoglycal.

The rearrangement, which was the most successful with tri-*O*-acetyl-D-glucal (**1**) and the least with tri-*O*-acetyl-D-galactal (**11**), parallels trends in the acid-catalyzed alcoholysis of these glycals studied by Ferrier and co-workers[16–18]. In the latter reaction, this observation was rationalized by the ability of the *trans* 4-acetoxyl group in **1** to provide anchimeric assistance. Thus, in the cases of **6** and **11**, where this assistance is not available, the allylic rearrangement competes less successfully with hydration of the double bond, and other acid-catalyzed reactions[19].

Isolation of the 5-acetates **4**, **9**, and **14** indicated that acetyl migration occurs from **3**, **8**, and **13** during the hydrolysis. Evidently, migration in these acyclic systems is a facile process owing to the ease with which the ortho-acid intermediates[20] are formed.

In summary, hydrolysis of acetylated glycals proceeds first to the acetylated pseudoglycals (**2**, **7**, and **12**) and then subsequently to the *aldehydo*-hex-2-enoses (**3**, **8**, and **13**). The conversion is accelerated by the presence of a small proportion of acetic acid, and is inhibited by the presence of hydroquinone. Isolation of the unsaturated aldehydes is best effected by peracetylating the hydrolyzate and then fractionating the mixture on dimethyl sulfoxide-impregnated paper.

EXPERIMENTAL

General. — Melting points were determined on a Fisher–Johns heating stage or a Mel–Temp apparatus, and are uncorrected. The p.m.r. spectra were determined, unless

otherwise stated, for solutions in chloroform-*d* containing 1% of tetramethylsilane as the internal standard, with either a Varian T-60, a Varian HA 100, or a Varian HR 220 spectrometer. Coupling constants were obtained by measuring spacings of spectra judged to be first-order.

Thin-layer chromatography was performed on glass plates coated with silica gel (HF 254, E. Merck) to a thickness of 0.3 mm. The chromatograms were first viewed under ultraviolet light, then exposed to iodine vapor, and finally sprayed with concentrated sulfuric acid. Heating in an oven was needed for complete visibilization. For column chromatography, Silica Gel (E. Merck, 0.05–0.20 mm, 70–325 mesh, A.S.T.M.) was used.

Preparation of dimethyl sulfoxide-impregnated papers was carried out as described by Wickberg[15], petroleum ether (b.p. 35–60°) being used as the eluant.

Tri-*O*-acetyl-D-glucal (**1**) and tri-*O*-acetyl-D-galactal (**11**) were prepared according to the literature[21,22] and di-*O*-acetyl-D-arabinal (**6**) was purchased from Raylo Chemicals Ltd., Edmonton, Alberta, Canada.

The acetylated pseudoglycals **2**, **7**, and **12** were prepared from the appropriate acetylated glycals by brief treatment with boiling water according to the published procedures[8,17].

Typical hydrolysis of acetylated glycals. — A solution of the acetylated glycal (1 mmole) in 1,4-dioxane (1–2 ml) was added to boiling water (5 ml). The solution was then boiled under reflux with efficient stirring, and the progress of the reaction was monitored by t.l.c. and p.m.r. (see later). Upon completion of the reaction, the mixture was allowed to cool and was then extracted with dichloromethane. The extract was successively washed with aqueous sodium hydrogen carbonate solution and water, dried (sodium sulfate), and evaporated to a syrup, which was purified on a column of silica gel with 1:1 petroleum ether–ethyl acetate as eluant, whereby the pseudoglycal and aldehyde were obtained as a mixture in yields of 46 to 85% (based on the acetylated glycal). Isolation of the unsaturated aldehyde was best accomplished by acetylating the crude products, and fractionating on dimethyl sulfoxide-impregnated paper[15]. The procedure is detailed for compound **5**.

Determination of reaction progress. — Results from various hydrolyses are shown in Tables I, II, and III, and Figs. 1, 2, and 3. The "percent conversions" were estimates from the p.m.r.-spectral studies (see Table IV), based on the intensities of H-1 of the aldehydes (**3**,**4**), (**8**,**9**) and (**13**,**14**) and H-2,H-3 of the pseudoglycals (**2**, **7**, and **12**) relative to the appropriate number of acetyl protons. The ratios of aldehyde to pseudoglycal were determined from the relative intensities of H-1 of the aldehydes to H-2 plus H-3 of the pseudoglycals.

1. Preparative reactions.

*Hydrolysis of tri-*O*-acetyl-*D*-glucal* (**1**). *Isolation of 4,5,6-tri-*O*-acetyl-*trans*-2,3-dideoxy-*aldehydo-D-erythro-*hex-2-enose* (**5**). — To boiling, distilled water (50 ml) was added a solution of compound **1** (2.5 g; 10 mmoles) in 1,4-dioxane (5 ml). The solution was boiled under reflux for 1.5 h, cooled, extracted with dichloromethane.

and the extract washed with saturated, aqueous sodium hydrogen carbonate, dried (sodium sulfate), and evaporated to dryness to yield an oil (2.0 g). T.l.c. with 1:1 petroleum ether–ethyl acetate revealed **3** and **4** as a u.v.-active spot of R_F 0.20. When the chromatograms were sprayed with sulfuric acid, the mixture of **3** and **4** gave a wine-red spot, and another major component which charred black (R_F 0.30) was detected. The latter was shown to be **2** by comparison with an authentic sample[5]. However, attempts to fractionate this mixture by chromatography on silica were unsuccessful.

A portion of the material (1.0 g) was dissolved in pyridine (5 ml) and acetylated overnight with acetic anhydride (2 ml) in a refrigerator (~10°). T.l.c. with 1:1 petroleum ether–ethyl acetate showed only one major, unresolved zone (R_F 0.52), the composite nature of which was evident from the fact that the upper portion charred wine-red, while the lower portion charred black. The former was also visible under u.v. light.

The mixture of acetates (0.250 g) was applied to a single sheet of Whatman 3MM paper which had been impregnated with dimethyl sulfoxide[15] and the chromatogram was developed with petroleum ether (b.p. 35–60°) for 12 h. The paper was dried, and the u.v.-active zone was cut out, and extracted with chloroform. The extract was freed of dimethyl sulfoxide by washing with water, dried, and evaporated, to give **5** (135 mg), $[\alpha]_D^{23}$ +12.0° (*c* 2.32, chloroform); lit.[14] $[\alpha]_D^{23}$ +25.3° (*c* 4.3, chloroform). The n.m.r., u.v., and i.r. spectral data for **5** are given in Table IV.

Compound **5** was characterized as its (2,4-dinitrophenyl)hydrazone, m.p. 108–109°; lit.[14] m.p. 111–112°; λ_{max} 370 nm (ε_{mM} 22.5).

Anal. Calc. for $C_{18}H_{20}N_4O_{10}$: C, 47.79; H, 4.42; N, 12.39. Found: C, 47.39; H, 4.36; N, 12.49.

4,5,6-Tri-O-*acetyl-2,3-dideoxy*-aldehydo-D-erythro-*hexose* (**16**). — Compound **5** (90 mg) in ethanol (10 ml) was hydrogenated in an ice–salt bath with 5% Pd/C as the catalyst. The uptake of hydrogen ceased after 7 ml (0.96 mole-equiv.) had been absorbed. The product (81 mg) showed $\nu_{max}^{CHCl_3}$ 2809 and 2740 cm^{-1} for the aldehydic C–H stretching.

Compound **16** was characterized as its (2,4-dinitrophenyl)hydrazone: m.p. 123–124°; λ_{max} 356 nm (ε_{mM} 18.2).

Anal. Calc. for $C_{18}H_{22}N_4O_{10}$: C, 47.57; H, 4.84; N, 12.34. Found: C, 47.43; H, 4.68; N, 12.20.

2,3-Dideoxy-D-erythro-*hexose* (**19**). — A portion (10 mg) of **16** was deacetylated with 2 ml of 5:4:1 methanol–water–triethylamine, and comparison of the product with authentic **19** (prepared from known[16,18] **18** by hydrolysis with 1% sulfuric acid) on paper chromatograms developed with 5:1:4 butanol–ethanol–water and made visible with the silver nitrate spray[23] showed that they were identical, R_F 0.74.

2. Analytical experiments. — These were performed on 1 mmolar quantities of tri-*O*-acetyl-D-glucal (**1**) as indicated in the section entitled "typical hydrolysis" and in Table I. The results are given in Table I and Fig. 1.

*Hydrolysis of ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-*D*-erythro-hex-2-enopyranoside* (**17**). — A solution of compound[16] **17** (1.0 g) in 1:1 water-1,4-dioxane (50 ml) was boiled under reflux for 24 h, and evaporated to a syrup which was dissolved in chloroform and the solution dried (sodium sulfate) and evaporated (0.74 g). Examination by the n.m.r. method already described showed that it consisted of the aldehydes **3** plus **4** and di-*O*-acetylpseudo-D-glucal (**2**) in the ratio of 3:2.

*Hydrolysis of di-*O*-acetyl-*D*-arabinal* (**6**). — The hydrolyses of **6** were conducted as described for tri-*O*-acetyl-D-glucal; the results are presented in Table II and Fig. 2. T.l.c. of the reaction product in 1:1 ethyl acetate–petroleum ether (b.p. 35–60°) revealed two poorly resolved spots of R_F ~0.16, and the pseudo-D-arabinal (**7**) at R_F ~0.27. Column chromatography on silica with the same solvent-system afforded fractions consisting of mainly one (**8**) or the other (**9**) isomer. On acetylation, both fractions afforded the same compound, **10** (R_F 0.6); for pure **10**, $[\alpha]_D^{23}$ +8.9° (*c* 1, chloroform). Spectroscopic data for **8**, **9**, and **10** are given in Table IV.

*Hydrolysis of tri-*O*-acetyl-*D*-galactal* (**11**). — The results from hydrolyses of **11** are given in Table III and Fig. 3. T.l.c. of the reaction product showed the two unsaturated aldehydes **13** and **14** (R_F 0.23 and 0.17), the pseudo-D-galactal (**12**) (R_F 0.28), and two faster-running spots, in addition to the unreacted starting-material (**11**). This mixture could not be resolved by column chromatography on silica. It was acetylated, and purified by chromatography on dimethyl sulfoxide-impregnated papers as described for tri-*O*-acetyl-D-glucal. Compound **15** thereby isolated was still contaminated with a minor amount (~10%) of an unknown compound. However, the identity of **15** was established by comparison of its n.m.r. parameters to those of **5** and **10** (see Table IV).

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NOTE ADDED IN PROOF

After this manuscript had gone to press, a paper by Gonzalez, Lesage, and Perlin appeared that described the formation of the unsaturated aldehydes **3** and **13** by mercuric ion-catalyzed reaction of D-glucal triacetate and D-galactal triacetate, respectively, with water[24]. In these reactions, the corresponding pseudoglycals, **2** and **12**, are not formed as intermediates, and the aldehydes are obtained in a high state of purity in almost quantitative yields.

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