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PHOTOCHEMICAL ADDITION OF 1,3-DIOXOLANE AND OF 2-PROPANOL TO 1,2,4,6-TETRA-*O*-ACETYL-3-DEOXY-α- AND -β-D-*erythro*-HEX-2-ENOPYRANOSE*

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ABSTRACT

Photoirradiation of a solution of 1,2,4,6-tetra-*O*-acetyl-3-deoxy-β-D-*erythro*-hex-2-enopyranose (**1**) in 1:50 acetone–1,3-dioxolane with a high-pressure mercury-lamp, followed by chromatographic separation, gave 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-*C*-(1,3-dioxolan-2-yl)-β-D-glucopyranose (**3**) (44%) and -mannopyranose (**4**) (35%). Similar treatment of the α anomer (**2**) of **1** afforded 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-*C*-(1,3-dioxolan-2-yl)-α-D-glucopyranose (**5**) (38%), -mannopyranose (**6**) (31%), and -allopyranose (**7**) (21%).

On the other hand, irradiation of **2** in 1:100 acetone–2-propanol gave 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-*C*-(1-hydroxy-1-methylethyl)-α-D-mannopyranose (**8**) (76%). Moreover, irradiation of **2** in 1:1 acetone–2-propanol yielded 1,4,6-tri-*O*-acetyl-3-deoxy-2,3-di-*C*-(1-hydroxy-1-methylethyl)-α-D-gluco- or -manno-pyranose $2,2^1,3^1$-orthoacetate (**10**) (15%), in addition to **8** (44%).

INTRODUCTION

We have reported effective, and stereoselective, photochemical addition-reactions of 1,3-dioxolane or 2-propanol to 3,4,6-tri-*O*-acetyl-D-glucal[2–4], 2-acetoxy-3,4,6-tri-*O*-acetyl-D-glucal[1,2,4], and methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside[4,5], respectively; of these three unsaturated sugar derivatives, the last was found to be the most reactive in the reactions[4]. We now report on the reaction of 1,2,4,6-tetra-*O*-acetyl-3-deoxy-β- (**1**) and -α-D-*erythro*-hex-2-enopyranose (**2**) with 1,3-dioxolane and with 2-propanol, respectively.

*Part XIV of a series: Synthetic Studies of Carbohydrate Derivatives by Photochemical Reactions. For Part XIII, see ref. 1.

RESULTS AND DISCUSSION

Photoirradiation of a solution of **1** in 1:50* acetone–1,3-dioxolane with a high-pressure mercury-lamp for 8 h, followed by column chromatography on silica gel, afforded 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-*C*-(1,3-dioxolan-2-yl)-β-D-glucopyranose (**3**) (44%) and 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-*C*-(1,3-dioxolan-2-yl)-β-D-mannopyranose (**4**) (35%); 5% of **1** was recovered unchanged. The structures of **3** and **4** were

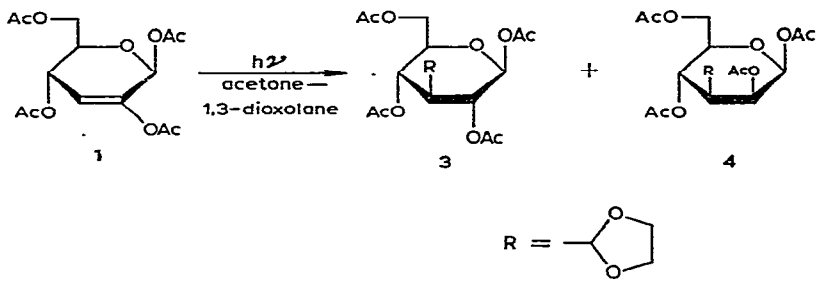


TABLE I

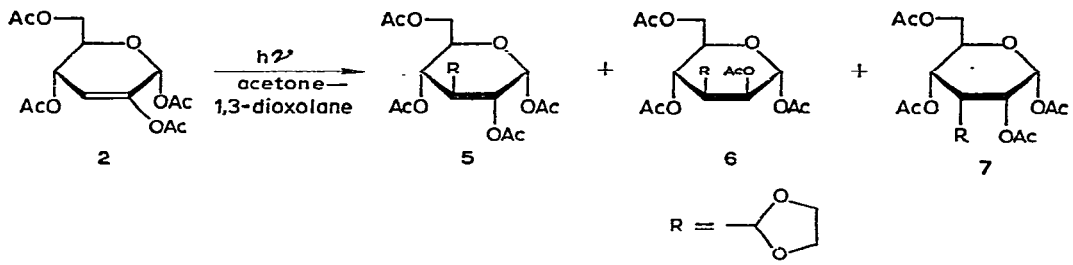
N.M.R. SPECTRAL DATA FOR COMPOUNDS **3**, **4**, **5**, **6**, AND **7**

3	**4**	**5**	**6**	**7**	*Assignment*
p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	
5.70 (d)	5.80 (d)	6.20 (d)	6.07 (d)	6.07 (d)	H-1
5.20 (dd)	5.53 (dd)	5.16 (dd)	5.21 (dd)	5.47 (t)	H-2
2.45 (td)	2.19 (ddd)	2.65 (dt)	2.37 (ddd)	2.30 (td)	H-3
5.31 (t)	5.34 (t)	5.25 (t)	5.45 (t)	5.23 (t)	H-4
~3.9 (m)	3.89 (m)		4.00 (ddd)		H-5
~4.2	4.32 (dd)	3.70–4.30	4.27 (dd)	4.1–4.4	H-6
	4.13 (dd)		4.07 (dd)		H-6′
4.83 (d)	4.87 (d)	4.85 (d)	4.78 (d)	5.06 (d)	H-2′
~3.87	~3.85	3.70–4.30	3.70–4.0	3.74–4.04	$-(CH_2)_2-$
2.01, 2.02, 2.04, 2.06	2.05, 2.05, 2.08, 2.15	2.00, 2.04, 2.07, 2.15	2.05, 2.06, 2.12, 2.13	2.05, 2.07, 2.07, 2.13	$OCOCH_3$
Coupling constants	**3** *Hz*	**4** *Hz*	**5** *Hz*	**6** *Hz*	**7** *Hz*
$J_{1,2}$	8.1	1.2	3.0	2.0	4.2
$J_{2,3}$	10.2	3.0	8.7	3.0	4.0
$J_{3,2'}$	2.7	6.5	1.8	6.5	6.5
$J_{3,4}$	10.2	11.0	8.3	10.5	6.1
$J_{4,5}$	10.2	10.0	8.3	10.5	
$J_{5,6}$		5.0		5.0	
$J_{5,6'}$		2.3		2.3	
$J_{6,6'}$		12.3		12.0	

*It is confirmed that it is appropriate to perform the photochemical addition-reaction in acetone–2-propanol or acetone–1,3-dioxolane by use[2] of the solvent ratio 1:9. However, judging from the standpoint of isolating products[1,6], the ratio of acetone to 2-propanol or to 1,3-dioxolane should be lowered

confirmed by the n.m.r.-spectroscopic evidence shown in Table I. The D-*gluco* configuration of **3** was assigned from the data for H-3 (δ 2.45; $J_{2,3}$ and $J_{3,4}$ 10.2 Hz) and for all of the acetyl methyl signals in the equatorial region[7]. The D-*manno* configuration of **4** was assigned from the data for H-3 (δ 2.19; $J_{3,4}$ 11.0 Hz and $J_{2,3}$ 3.0 Hz), and for one of the acetyl methyl signals in the axial region (δ 2.15)[7].

Similar photoirradiation of **2** in 1:50 acetone–1,3-dioxolane for 12 h, followed by chromatographic separation, gave 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-*C*-(1,3-dioxolan-2-yl)-α-D-glucopyranose (**5**) (38%), 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-*C*-(1,3-dioxolan-2-yl)-α-D-mannopyranose (**6**) (31%), and 1,2,4,6-tetra-*O*-acetyl-3-



deoxy-3-*C*-(1,3-dioxolan-2-yl)-α-D-allopyranose (**7**) (21%). The structures of these products were confirmed by the n.m.r.-spectroscopic evidence shown in Table I. The α-D-*gluco* configuration of **5** was assigned from the data for H-3 (δ 2.65; $J_{2,3}$ 8.7 Hz and $J_{3,4}$ 8.3 Hz), and for one of the acetyl methyl signals in the axial region (δ 2.15)[7]. The α-D-*manno* configuration of **6** was assigned from the data for H-3 (δ 2.37; $J_{3,4}$ 10.5 Hz and $J_{2,3}$ 3.0 Hz) and 1- and 2-*O*-acetyl methyl signals of the four in the axial region (δ 2.12 and 2.13, respectively)[7]. The α-D-*allo* configuration of **7** was assigned from the data for H-3 (δ 2.30; $J_{1,2}$ 4.2, $J_{2,3}$ 4.0, and $J_{3,4}$ 6.1 Hz, respectively) and for one of the four acetyl methyl signals in the axial region (1-*O*-acetyl: δ 2.13)[7]. [Incidentally, the values of $J_{1,2}$ and $J_{2,3}$ of **7** are also assignable to vicinal, equatorial protons, *i.e.*, those of the α-D-*altro* configuration, in which the substituents at C-1, C-2, and C-3 should have an axial orientation; this would make it difficult for compound **7** to assume the $^4C_1$(D) conformation, because of the bulkiness of the 1,3-dioxolan-2-yl group[6], and, thus, it would take the $^1C_4$(D) conformation. However, this conformation should give $J_{1,2}$ and $J_{2,3}$ values > 8.0 Hz, corresponding to protons in axial–axial relationship; therefore, it was concluded that **7** has, not the α-D-*altro*, but the α-D-*allo* configuration.]

As already described, compounds **1** and **2** are, as expected, sufficiently reactive to give products having the 1,3-dioxolan-2-yl substituent regiospecifically attached at C-3 and being stereochemically more stable. The stereoselectivity of these reactions was clearly demonstrated by the order for the 2-*O*-acetyl-3-*C*-(1,3-dioxolan-2-yl) derivatives: (2*e*,3*e*) [**3** (44%) and **5** (38%)] > (2*a*,3*e*) [**4** (35%) and **6** (31%)] > (2*e*,3*a*) [**7** (21%)].

The addition reaction of 2-propanol to the enoses was next investigated. Photoirradiation of a solution of **1** in 1:100 acetone–2-propanol induced the reaction

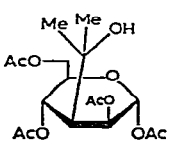
TABLE II

N.M.R. SPECTRAL DATA FOR COMPOUNDS **8** AND **10**

8	**10**	*Assignment*
p.p.m.	*p.p.m.*	
5.97 (d)	5.99 (s)	H-1
5.22 (t)		H-2
2.45 (dd)	2.51 (d)	H-3
5.44 (dd)	5.22 (t)	H-4
3.7–4.2	3.7–4.3	H-5, H-6, H-6′
2.07, 2.10, 2.14, 2.15	2.05, 2.13, 2.15	$OCOCH_3$
1.24, 1.30	1.14, 1.24, 1.52, 1.54, 1.55	$C\text{-}CH_3$
Coupling constant	**8**	**10**
	Hz	*Hz*
$J_{1,2}$	2	
$J_{2,3}$	3	
$J_{3,4}$	12.0	8.0
$J_{4,5}$	9.0	8.0

very effectively, despite the somewhat smaller proportion of acetone. T.l.c. and g.l.c. of the reaction mixture revealed the disappearance of the starting material, even after only 9 h, and the formation of many products. Moreover, g.l.c. indicated transformation, during the irradiation, of a product initially formed into an unexpected product. Expectedly, separation of the products was unsuccessful, although resolution by chromatography (column and preparative, thin-layer) was repeatedly attempted. This behavior parallels that in photoinduced addition-reactions to furanosyl derivatives, *e.g.*, methyl 5-deoxy-2,3-*O*-isopropylidene-*β*-D-*erythro*-pent-4-enofuranoside[4,8] and 1,2:5,6-di-*O*-isopropylidene-3-deoxy-*α*-D-*erythro*-hex-3-enofuranose[9]. These enofuranose derivatives, also, are sufficiently reactive to be used up during short irradiation, the main reaction being accompanied by some side and secondary reactions, and, therefore, they give more products than expected, with low selectivity, making the isolation of products extremely difficult.

Similar irradiation of a solution of **2** in 1:100 acetone–2-propanol for 16 h, followed by chromatography, gave a 76% yield of 1,2,4,6-tetra-*O*-acetyl-3-deoxy-3-*C*-(1-hydroxy-1-methylethyl)-*α*-D-mannopyranose (**8**); 18% of **2** was recovered unchanged. The structure of **8** was assigned from the n.m.r.-spectroscopic evidence shown in Table II; the data for H-3 (δ 2.45; $J_{3,4}$ 12 Hz and $J_{2,3}$ 3 Hz) and for two



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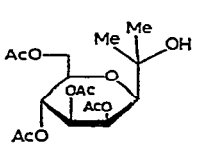

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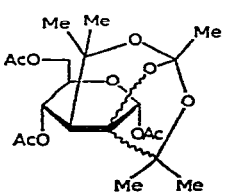

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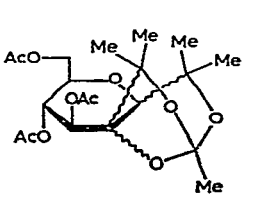

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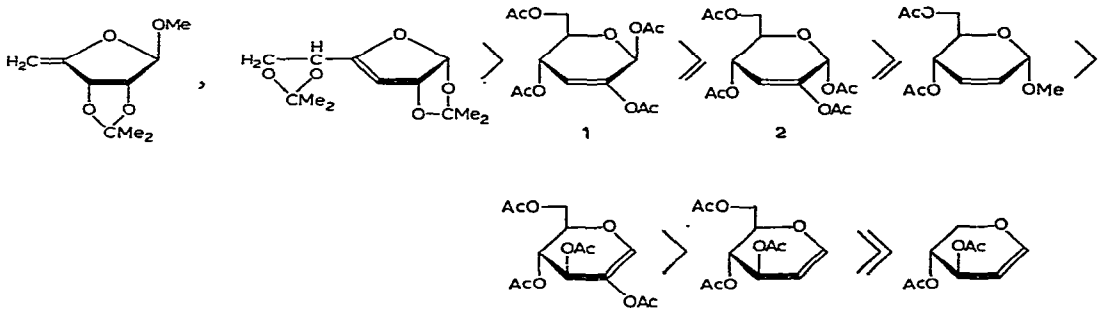
of the acetyl methyl signals in the axial region (δ 2.14 and 2.15, respectively)[7] indicated the α-D-*manno* configuration. The highly stereoselective formation of **8** in this reaction, in contrast with the poor stereoselectivity observed in the reaction of **1**, is interesting. Compound **2** seems to have moderate reactivity towards 2-propanol, and gave no D-*gluco* type of product, in comparison with the reaction with 1,3-dioxolane. Rosenthal and Ratcliffe[10] reported the isolation of **8** (6.9%) as a byproduct in the photoamidation of **2** in formamide in the presence of acetone, its formation involving a side addition-reaction of (1-hydroxy-1-methylethyl) radical to **2**. In the previous papers of this series, it has, moreover, been revealed that, when the photochemical additions are highly stereoselective, they favor formation of an isomer stereochemically less hindered and/or thermodynamically more stable. These facts permit interpretation of the stereoselectivity (to give mainly **8**) as follows: the first step involves the attack of the (1-hydroxy-1-methylethyl) radical on the less substituted C-3 atom of **2**, giving an intermediary, C-2 radical having the (1-hydroxy-1-methylethyl) substituent equatorially oriented, and the second step may, on abstraction of hydrogen radical from 2-propanol, determine the axial orientation of the 2-acetoxyl group, which may arise from potential stabilization by hydrogen bonding between the carbonyl oxygen atom and the hydroxyl group of the substituent on C-3. By such an interpretation, the formation of the D-*glycero*-D-*galacto* isomer (**9**) (21% yield), as well as the D-*glycero*-D-*gulo* isomer (51.2% yield), in the addition of 2-propanol to 2-acetoxy-3,4,6-tri-*O*-acetyl-D-glucal[1] is rationalized; the (1-hydroxy-1-methylethyl) group introduced on C-1 may also potentially interact with the ring oxygen atom, giving two products, and thus differing from the reaction of **2**.

On increasing the proportion of acetone to 2-propanol, the reaction of **2** was found by t.l.c. and g.l.c. to give a product other than **8**. The reaction of **2** in 1:1 acetone–2-propanol was performed for 16 h, and followed by chromatographic separation, giving 1,4,6-tri-*O*-acetyl-3-deoxy-2,3-di-*C*-(1-hydroxy-1-methylethyl)-α-D-gluco- or -manno-pyranose $2,2^1,3^1$-orthoacetate (**10**) (15% yield), in addition to **8** (44% yield). The structure of **10** was confirmed by ^{1}H- (shown in Table II) and ^{13}C-n.m.r. (see Experimental section) data. The former spectrum showed no signal corresponding to H-2, $J_{3,4}$ and $J_{4,5}$ both 8 Hz, only three acetyl methyl signals, and three of the five *C*-methyl signals (δ 1.52, 1.54, and 1.55, respectively). The latter spectrum had a signal for orthocarbonyl carbon at δ 118.6; one of the three *C*-methyl proton signals that appeared at lower field may correspond to that located on this carbonyl carbon atom. Incidentally, the orthoacetate **11**, obtained from the reaction of 2-acetoxy-3,4,6-tri-*O*-acetyl-D-glucal gave the *C*-methyl proton signal of the orthoacetyl group at δ 1.55 (^{1}H-n.m.r.) and the orthocarbonyl carbon signal at δ 117.27 (^{13}C-n.m.r.)[1], which agree with those of **10**. Therefore, it may be assumed that **10** is formed by the addition of two (1-hydroxy-1-methylethyl) radicals to **2** followed by formation of the orthoacetate by the photochemical process[1].

In conclusion, compounds **1** and **2** have excellent reactivity in the photochemical addition-reactions. It is noteworthy that **1** is especially reactive (next to the enose derivatives having a five-membered ring structure). Therefore, **1** will be useful

for the preparation of branched-chain sugar derivatives by such kinds of photochemical addition-reaction.

A survey of all of the experimental results, reaction conditions, and chromatographic aspects thus far reported indicates, by and large, an order of reactivity in the photochemical addition-reactions of unsaturated sugar derivatives as follows[4,6,9]:



The reverse order may approximately be adopted to interpretation of the stereoselectivity observed in the reactions of these unsaturated sugar derivatives, although the predominant formation of **8** constitutes an exceptional case.

EXPERIMENTAL

General. — Acetone and 2-propanol were purified as usual. 1,3-Dioxolane was prepared from ethylene glycol and paraformaldehyde, according to the established method[11], and purified. Compounds **1** and **2** were prepared according to the method of Ferrier *et al.*[12]. A solution of each of the unsaturated sugar derivatives was placed in a Pyrex-glass test-tube, which was tightly stoppered after passing argon gas through the solution for ~30 min. Irradiations were conducted externally, at a distance of ~5 cm, with a 450-W, high-pressure, mercury lamp (Ushio Electric Inc.), the tubes and the lamp being cooled with running water during the irradiation. T.l.c. was performed on Merck TLC aluminum sheets coated with Silica gel 60 F_{254}, with 9:1 (v/v) benzene–methanol as the developer. G.l.c. was performed with a Hitachi Model K-53 instrument on a column of 10% of SE-30 on Chromosorb-W (60–80 mesh), with nitrogen at 1.5 atm. as the carrier gas; oven temperature, 200°, and injection temperature, 300°. All retention times are given with reference to those of compounds **1** and **2** as unity. Specific rotations were calculated by the Drude equation in terms of α_{546} and α_{578}, determined with a Carl Zeiss Photoelectric Precision Polarimeter (±0.005°). ^{1}H-N.m.r. spectra were recorded with a Varian EM-390 instrument for solutions in deuteriochloroform, with tetramethylsilane as the internal standard, and the spectra obtained were analyzed by the double-resonance and/or INDOR technique. ^{13}C-N.m.r. spectra were recorded with a Varian CFT-20 instrument for solutions in deuteriochloroform, with tetramethylsilane as the internal standard. All melting points are uncorrected.

*1,2,4,6-Tetra-*O*-acetyl-3-deoxy-3-*C*-(1,3-dioxolan-2-yl)-β-*D*-gluco- and -manno-*

pyranose (**3** *and* **4**). — A solution of 1,2,4,6-tetra-*O*-acetyl-3-deoxy-β-D-*erythro*-hex-2-enopyranose (**1**; 200 mg) in acetone (0.2 mL)–1,3-dioxolane (10 mL) was irradiated with the u.v. lamp for 8 h. The resulting solutions (in ten test tubes) were combined and evaporated; total weight of **1** used, 2 g. The resulting, syrupy mixture was chromatographed on a column (3 × 30 cm) of silica gel (Wakogel C-300); successive elution with 99:1 (1 L), 49:1 (1.5 L), and 19:1 benzene–acetone (1 L), and 49:1 benzene–methanol (500 mL) gave, in turn, **1** (107 mg, 5% recovery), **3** (377 mg), a mixture of **3** and **4** (1.053 g), and **4** (477 mg). As the isolated **3** crystallized instantly after separation, the mixture of **3** and **4** was repeatedly dissolved in diethyl ether and the solution nucleated with crystals of **3** (to crystallize out **3** from the solution). Totals of 1.070 g (44% yield) of **3** and 850 mg (35% yield) of **4** were obtained. It was impossible to distinguish between compounds **3** and **4** by t.l.c. or g.l.c., but possible by n.m.r. spectroscopy; n.m.r. data for **3** and **4** are given in Table I. Compound **3** had m.p. 119–121° (diethyl ether); $[\alpha]_D^{22}$ of **3**, 0° (*c* 1.0, acetone), and of **4** −20° (*c* 1.0, acetone); R_F values in t.l.c.: **3** and **4**, both 0.65 (**1**, 0.80); retention times in g.l.c.: **3** and **4**, both 2.1 (**1**, 1.0).

Anal. Calc. for $C_{17}H_{24}O_{11}$: C, 50.49; H, 5.98. Found: for **3**, C, 50.61; H, 5.98; for **4**, C, 50.63; H, 6.06.

1,2,4,6-Tetra-O-*acetyl-3-deoxy-3*-C-(*1,3-dioxolan-2-yl*)-α-D-*glucopyranose*, -α-D-*mannopyranose, and* -α-D-*allopyranose* (**5**, **6**, *and* **7**). — A solution of 1,2,4,6-tetra-*O*-acetyl-α-D-*erythro*-hex-2-enopyranose (**2**) (200 mg) in acetone (0.2 mL)–1,3-dioxolane (10 mL) was irradiated in a test tube for 12 h. The resulting solutions in five tubes were combined (total weight of **2** used, 1 g), and evaporated *in vacuo* to a syrup. The syrupy residue was chromatographed on a column (3 × 30 cm) of silica gel, eluting successively with benzene (500 mL), and 99:1 (1 L), 49:1 (1 L), and 19:1 benzene–acetone (1 L), to give **6** (85 mg), a mixture of **5**, **6**, and **7** (1.015 g), and **7** (35 mg). Compound **7** crystallized at once after the separation. A further 80 mg of crystalline **7** was obtained on nucleating (with a crystal of **7**) the diethyl ether solution (10 mL) of a fraction (~200 mg) containing much **7**. The fractions (~550 mg) containing much **5** were dissolved in diethyl ether (30 mL); on standing the solution gave 255 mg of crystalline **5**. Repeated column-chromatographic separation and crystallization of the syrupy residue gave totals of 470 mg (38% yield) of **5**, 380 mg (31% yield) of **6**, and 260 mg (21% yield) of **7**. Differentiation of these isomers was impossible by t.l.c. and g.l.c., but possible by n.m.r. spectroscopy. N.m.r. data for **5**, **6**, and **7** are given in Table I. M.p. of **5**, 140.5–141° (diethyl ether), and of **7**, 169–170° (diethyl ether); $[\alpha]_D^{22}$ of **5** +40.2° (*c* 1.0, acetone), of **6** +37.4° (*c* 1.0, acetone), and of **7** +14° (*c* 1.0, acetone); R_F values in t.l.c.: **5**, **6**, and **7**, 0.75 (**2**, 0.90); retention times in g.l.c.: **5**, **6**, and **7**, 2.2 (**2**, 1.0).

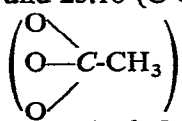
Anal. Calc. for $C_{17}H_{24}O_{11}$: C, 50.49; H, 5.98. Found: for **5**, C, 50.77; H, 6.00; for **6**, C, 50.70; H, 5.94; and for **7**, C, 50.56; H, 5.92.

1,2,4,6-Tetra-O-*acetyl-3-deoxy-3*-C-(1-*hydroxy-1-methylethyl*)-α-D-*manno-pyranose* (**8**). — A solution of **2** (400 mg) in acetone (0.2 mL)–2-propanol (25 mL) was similarly irradiated for 30 h, and the resulting solution was evaporated *in vacuo*

to a syrup. The residue was chromatographed on a column (3 × 20 cm) of silica gel, with successive elution with 199:1 (1.5 L) and 99:1 benzene–methanol (2 L), to give, in turn, **2** (70 mg, 18% recovery), structurally unestablished compound (30 mg), and **8** (360 mg, 76% yield). Compound **8** crystallized on standing; its n.m.r. data are given in Table II. M.p. of **8**, 92–94° (diethyl ether), $[\alpha]_D^{22}$ +16.5° (*c* 1.0, acetone); R_F value in t.l.c.: **8**, 0.61 (**2**, 0.90); retention time in g.l.c.: **8**, 1.4 (**2**, 1.0).

Anal. Calc. for $C_{17}H_{26}O_{10}$: C, 52.30; H, 6.71. Found: C, 52.44; H, 6.79.

1,4,6-Tri-O-*acetyl-3-deoxy-2,3-di*-C-(*1-hydroxy-1-methylethyl*)-α-D-*gluco-* (*or* -D-*manno-*)*pyranose* (**10**). — A solution of **2** (400 mg) in acetone (12 mL)–2-propanol (12 mL) was irradiated in the same way for 30 h, and the resulting solution was evaporated *in vacuo* to a syrup. This was chromatographed on a column (3 × 20 cm) of silica gel, eluting successively with 997:3 (1 L), 199:1 (1 L), and 99:1 benzene–methanol (2 L), to give **10** (75 mg, 15% yield) and **8** (210 mg, 44%). Product **10** was contaminated by a trace of **2**; $[\alpha]_D^{22}$ +30.6° (*c* 1.0, acetone); R_F value in t.l.c.: **10**, 0.85 (**2**, 0.90); retention time in g.l.c.: **10**, 2.0 (**2**, 1.0). The n.m.r.-spectral data for **10** are given in Table II; ^{13}C-n.m.r.: δ 91.16 (C-1); 82.61, 81.49, and 73.68 (C-2,2^1,3^1); 42.98 (C-3); 69.38 and 67.47 (C-4 and C-5); 63.52 (C-6); 32.54, 29.20, 24.94, 24.31, and 23.18 (C-*C*H$_3$'s); 21.32, 20.72, and 20.72 (OCO*C*H$_3$'s); and 118.06



Anal. Calc. for $C_{20}H_{30}O_{10}$: C, 55.80; H, 7.03. Found: C, 55.74; H, 6.93.

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