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DIOXOLANE AND DIOXANE ACETAL DERIVATIVES OF D-ALLOSE: CONDENSATION OF 3-*O*-BENZYL-D-ALLOSE WITH ACETALDEHYDE*

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ABSTRACT

Condensation of 3-*O*-benzyl-D-allose with acetaldehyde forms a complex mixture from which potentially useful mono- and di-*O*-ethylidene derivatives were isolated and identified. Compounds isolated and identified after conversion of unsubstituted hydroxyl groups into the corresponding acetates included 1,2-di-*O*-acetyl-3-*O*-benzyl-4,6-*O*-ethylidene-β-D-allopyranose; 5,6-di-*O*-acetyl-3-*O*-benzyl-1,2-*O*-(*R*)-ethylidene-α-D-allofuranose; and two 3-*O*-benzyl-1,2:5,6-di-*O*-ethylidene-α-D-allofuranoses, both having the *R* configuration in the 1,2-*O*-ethylidene ring. Furanose and pyranose conformations were determined by n.m.r. analysis, and the location and configuration of each acetal ring was established. The benzyl ether group in the furanose derivatives was removed by catalytic hydrogenation with subsequent formation of 3-*O*-acetyl analogs.

INTRODUCTION

Acetone and acetaldehyde form analogous 2,3:5,6-di-*O*-alkylidene-β-D-allofuranose derivatives[1–3], even though similar condensations of acetaldehyde with other monosaccharides often produce 1′,3′-dioxane ring derivatives[4,5]. Furthermore, under conditions of moderate acidity, the favored existence of 2,3:5,6-substituted forms causes rearrangement of such otherwise stable derivatives as 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose[2]. For this reason, despite a wide variety of potential acetals of D-allose, derivatives other than 2,3:5,6-substituted forms have been prepared only indirectly from analogous D-hexose acetals; for example, methyl 4,6-*O*-benzylidene-α-D-allopyranoside[6] and 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose[7].

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*Part II of a series on D-allose acetals. For Part I, see ref. 3.

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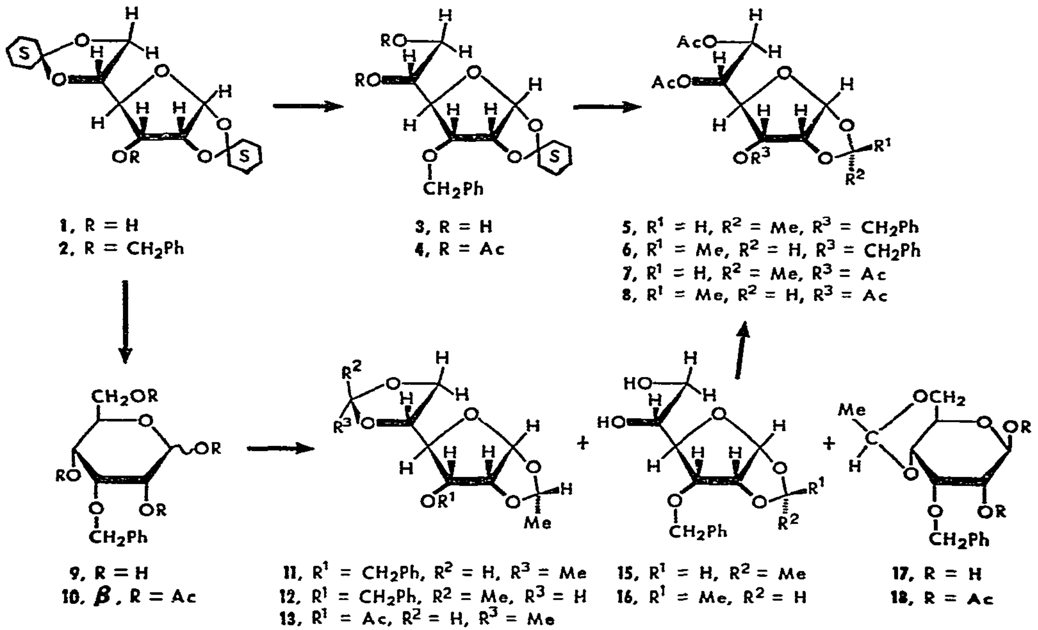
DISCUSSION

Protecting O-3 as the benzyl ether offers a simple way to prevent formation of 2,3:5,6-diacetal derivatives of D-allose, as the ether is stable to the reaction conditions and is easily removed by hydrogenation. Furthermore, condensation of 3-*O*-benzyl-D-allose with acetaldehyde can be expected to give dioxolane and dioxane acetal derivatives containing furanose or pyranose rings, whereas condensations with acetone would be more likely to form the usual 1,2-*O*- and 1,2:5,6-di-*O*-substituted furanoses.

Preparation of 3-*O*-benzyl-D-allose (9) is shown in the scheme. Synthesis of the immediate precursor (2) was straightforward, but subsequent hydrolysis in aqueous acetic acid to produce 9 was complicated by the formation of an unknown component in yields of 40–60%. The latter afforded compound **10** on acetylation and it had an n.m.r. spectrum consistent with a monoacetate of 9. A structure for the unknown product was not established.



1, R = H
2, R = CH_2Ph

3, R = H
4, R = Ac

5, R^1 = H, R^2 = Me, R^3 = CH_2Ph
6, R^1 = Me, R^2 = H, R^3 = CH_2Ph
7, R^1 = H, R^2 = Me, R^3 = Ac
8, R^1 = Me, R^2 = H, R^3 = Ac

9, R = H
10, β, R = Ac

11, R^1 = CH_2Ph, R^2 = H, R^3 = Me
12, R^1 = CH_2Ph, R^2 = Me, R^3 = H
13, R^1 = Ac, R^2 = H, R^3 = Me
14, R^1 = Ac, R^2 = Me, R^3 = H

15, R^1 = H, R^2 = Me
16, R^1 = Me, R^2 = H

17, R = H
18, R = Ac

SCHEME 1

Condensation of 9 with acetaldehyde produced complex mixtures, whether or not the syrupy 9 was dissolved in a solvent (such as methyl sulfoxide) before the other reagents were added. T.l.c. examination of the products showed small amounts of unreacted 9 and three pairs of compounds having markedly different R_F values: two pairs of spots having chromatographic mobilities similar to standard mono- and di-*O*-ethylidene-D-glucoses and two spots of intermediate mobility. Formation of materials having low or intermediate R_F values was favored when quantities of acetaldehyde were decreased to a level equimolar with that of **9**, but all compounds detected in reactions with higher concentrations of acetaldehyde were also present, including minor by-products. The three groups of compounds were separated by column chromatography.

The fraction of low R_F was a mixture of monoethylidene acetals, of which approximately one-third was **17**. The remainder was largely **15**, with small proportions of **16** and two unidentified by-products.

Structures of the major monoethylidene acetals were established by n.m.r.-spectral examination of their derived acetals, **5** and **18** (Table I).

For **18**, the vicinal proton coupling-constants are consistent with a β-D-allopyranose ring in the $^4C_1$ chair conformation. The observed mutarotation also indicates the β-D-configuration for **17**, but the small magnitude of the positive increase in rotation suggests that the α-D-form is disfavored.

Location of the acetal ring in **5** was straightforward from the n.m.r. spectra, as was the assignment of the *O*-acetyl groups. The *R* configuration was established for C-2′ of the 1,2-*O*-ethylidene ring by application of well-established principles that relate the chemical shift of a C-2′ proton on a 1′,3′-dioxolane ring to interactions with 4′-*cis*-5′-dialkyl substituents[8–12]. Samples of **5** and **6** were available for comparison, having been prepared in 93:7 ratio from **4**. Because the vicinal proton coupling-constants recorded for **2**, **4**, **5**, and 1,2:5,6-di-*O*-isopropylidene-α-D-allose[13] are almost equal, the conformations of the furanose rings must be similar.

The two compounds having the highest chromatographic mobility were separated by preparative t.l.c., crystallized, and identified as the diastereoisomeric 3-*O*-benzyl-1,2:5,6-di-*O*-ethylidene-α-D-alloses (**11** and **12**). Assignment of the acetal-ring locations was made by n.m.r. spectroscopy after a C-4–C-5 cleavage pattern unique to furanoses[14] had been recognized in the mass spectrum of each isomer. Subsequent partial hydrolysis of each isomer, followed by acetylation, yielded **5** from each, and established the configuration of C-2′ in the 1,2-*O*-ethylidene ring as *R* in **11** and **12**. Small proportions of **6** (6–8%) were noted in the hydrolyzed, acetylated samples, presumably arising from configurational scrambling during hydrolysis, as no evidence for 1,2-*O*-(*S*)-forms was observed in the n.m.r. spectra of **11** and **12**.

Assignment of the 5,6-*O*-ethylidene ring configuration in **11** and **12** as *R* and *S*, respectively, was essentially as described for **5**, where the highest-field methine quartet (C-2′ proton) associated with the 5,6-*O*-ethylidene resonances was assigned as *R*. Methine quartets centered at τ 5.00 and 5.02 were considered to be the C-2′ proton resonances of the 1,2-*O*-ethylidene rings.

Cleavage of the 3-benzyl ethers by catalytic hydrogenation was accomplished readily for **5**, **11**, and **12**. Partial cleavage of the 5,6-*O*-ethylidene ring was noted for **11** and **12**, as subsequent acetylation afforded small amounts of **7** from those samples, as well as **13** and **14**. The structures of **7**, **13**, and **14** were confirmed by n.m.r. spectroscopy.

The two products of intermediate chromatographic mobility formed when **9** is condensed with acetaldehyde were not identified. When examined as a mixture

TABLE I

N.M.R. PARAMETERS FOR 3-*O*-BENZYL D-ALLOSE DERIVATIVES[a]

Compound	*Solvent*	*Chemical shift, τ*				O-*Ethylidene ring*		*Ph-CH₂*	*Coupling constants, J (Hz)*				
		H-1	*H-2*	*H-3*	*H-4*	*2′-H*	*2′-CH₃*		$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	J_{CH_3-CH}
2	$CDCl_3$	4.26d	5.46t	6.15dd				5.43q	3.9	4.7	8.5		
4	CCl_4	4.36d	5.51t	6.26dd				5.50q	3.8	4.3	9		
5	C_6D_6	4.53d	5.97t	6.30dd		5.02q	8.66d	5.49q	4	4.5	9		5
6	C_6D_6					4.68q	8.73d						
7	C_6D_6	4.48d	5.43–5.58m	5.13dd		5.06q	8.70d		4.1	4.8	9		5
8	C_6D_6					4.77q	8.77d						
11	C_6D_6	4.51d	6.00dd	6.25dd		5.00q, 5.10q	8.64d, 8.69d	5.46	4	4.5	8.2		5, 5
12	C_6D_6	4.57d	6.09dd	6.55dd		4.92q, 5.02q	8.66d, 8.70d	5.55q	4	4.5	8.2		5, 5
13	C_6D_6	4.38d	5.47dd			4.99q, 5.09q	8.67d, 8.69d		4	5			5,5
14	C_6D_6	4.40d	5.48dd	5.25dd		4.89q, 5.00q	8.67d, 8.74d		4	5	8.5		5, 5
10	C_6D_6	3.57d	4.94dd	5.65t	5.00dd			5.55s	8.5	2.8	2.8	10	
17	Me_2SO-d_6	5.27[b]	6.76dd			5.27[b]	8.78d	5.29s	7	3			5
18	C_6D_6	3.64d	5.10dd	5.84t	6.98dd	5.73q	8.75d	5.32q	8.5	3	2.3	9.2	5

[a] 100 MHz; d = doublet, dd = doublet of doublets, m = multiplet, q = quartet, s = singlet, t = triplet. [b] Multiplicity obscured.

by n.m.r. spectroscopy, however, two *O*-ethylidene resonances were noted in an approximate ratio of 2:3 (low-field quartet:high-field quartet). The presence of 1,6-anhydro rings in these unknown products is possible, as strongly acidic conditions prevailed during acetal formation.

EXPERIMENTAL

General methods. — N.m.r. spectra were recorded at 100 MHz on a Varian HA-100 spectrometer with tetramethylsilane ($\tau = 10.0$) as the internal standard. Solute concentrations were approximately 20% (w/v or v/v). Chemical shifts and coupling constants are first-order, measured directly from spectral spacings. A Hewlett–Packard research chromatograph, Model 5750 equipped with an electronic integrator, was used for g.l.c. The column was 8 ft of 1/8-in. (o.d.) stainless-steel tubing packed with 3% HI-EFF 8BP (cyclohexanedimethanol succinate, Applied Science Labs) on Chromosorb W (80–100 mesh). Operation was isothermal with helium as the carrier gas and with flame-ionization detection.

Melting points were determined in capillary tubes. Optical rotations were recorded at 546.1 nm in a 0.2-dm cell with a Bendix recording polarimeter. Model 1169 Multiplication of the specific rotations by 0.85 allows comparison with values reported at the D-line of a sodium lamp. Solutions were evaporated under diminished pressure. Precoated plates of Silica Gel F-254 (E. Merck, Darmstadt, Germany) were used for t.l.c. Layer thickness was 0.25 mm for analytical separations and 2.0 mm for preparative. For column chromatography, Baker Analyzed Silica Gel No. 3405 (J. T. Baker Chemical Co.) was used without pretreatment. All chromatographic solvents were proportioned on a v/v basis. Calcium hydride was used to dry methyl sulfoxide.

3-O-Benzyl-1,2:5,6-di-O-cyclohexylidene-α-D-allose (**2**). — A 75-g portion of **1**, prepared essentially as described by Kawana and coworkers[15], was dissolved in *N,N*-dimethylformamide (400 ml) and stirred at 25° under nitrogen while being treated with two 9-g portions of sodium hydride (60% in mineral oil) at 0.5-h intervals. Stirring was continued for 2 h longer before the flask was stoppered and stored for 18 h. The mixture was then cooled and maintained at +10° with stirring while a solution of benzyl bromide (100 ml) in *N,N*-dimethylformamide (50 ml) was added dropwise during 0.5 h. Cooling was then discontinued and the mixture was stirred for an additional 4 h at 25° followed by final storage for 18 h. T.l.c. (benzene–ether 17:3) indicated almost complete conversion of **1** into **2**. The mixture was diluted with an equal volume of ether and filtered; the filtrate was evaporated at 80°. The residue was extracted with ethyl acetate (1000 ml), washed with water, and evaporated. Noncarbohydrate materials were removed from the crude syrup by dissolving the mixture in *n*-hexane (1000 ml) and chromatographing it on a column of silica gel (500 g) packed and eluted with *n*-hexane. Subsequent elution with 4:1 hexane-ether gave **2** as a syrup. A 1-g portion was repurified by preparative t.l.c. (9:1 benzene–ether, 1 ascent) and then distilled (250°/0.1 mtorr). This syrup had $[\alpha]_{546}^{27}$ +108° (*c* 1.6, chloroform).

Anal. Calc. for $C_{25}H_{34}O_6$: C, 69.74; H, 7.96. Found: C, 69.80; H, 8.19.

5,6-Di-O-acetyl-3-O-benzyl-1,2-O-cyclohexylidene-α-D-allose (**4**). — Hydrolysis of **2** (90 g) in aqueous methanol (1:5, 1200 ml) at 55° by *p*-toluenesulfonic acid (1 g) was monitored by t.l.c. (ethyl acetate). Samples were checked at 1-h intervals until **9** was detected (8 h), at which time sodium hydrogen carbonate (2 g) was added and the final solution evaporated. The residue was transferred to a separatory funnel with ethyl acetate (500 ml) and water (300 ml), the layers were separated, and each was evaporated. Crude **9** (3 g) was extracted with acetone from the residue of the aqueous layer.

The residue from ethyl acetate was chromatographed on silica gel with benzene as the eluent until all of compound **2** was recovered, and then with 17:3 benzene–ether to remove **3** (65 g). A 30-g portion of **3** was then kept for 48 h at 25° in acetic anhydride–pyridine (30 ml, 15 ml) and then evaporated; the residue was distilled (240°/0.1 mtorr) to yield **4**; $[\alpha]^{25}_{546}$ +115.5° (*c* 1, chloroform).

Anal. Calc. for $C_{23}H_{30}O_8$: C, 63.58; H, 6.96. Found: C, 63.70; H, 7.00.

5,6-Di-O-acetyl-3-O-benzyl-1,2-O-ethylidene-α-D-alloses (**5**, **6**). — A solution of **4** (30 g) in 90% aqueous trifluoroacetic acid (100 ml) was kept for 0.5 h at 25° and then evaporated rapidly at 40°. T.l.c. (9:1 chloroform–acetone,) showed that approximately 50% of the original amount of **4** had hydrolyzed. Extraction with cold hexane removed 4 and the insoluble residue was then crystallized from ether, and the 5.5 g of product was treated with paraldehyde (5 ml) and sulfuric acid (0.1 g) at 30° without further examination. Water collected at the bottom of the flask within 15 min, at which time anhydrous cupric sulfate (2 g) was added. The flask was stoppered and shaken for 1 h to complete the reaction (t.l.c., ether). The mixture was then filtered into ether (100 ml), stirred with anhydrous potassium carbonate (2 g) for 2 h, and refiltered. Low-boiling volatile materials were evaporated off, and the residue was then distilled (200°/0.1 mtorr) to yield a syrupy diastereoisomeric mixture of **5** and **6** (93:7 by n.m.r.); $[\alpha]^{27}_{546}$ +117° (*c* 1.7, chloroform).

Anal. Calc. for $C_{19}H_{24}O_8$: C, 59.99; H, 6.36. Found: C, 60.16; H, 6.31.

3-O-Benzyl-D-allose (**9**). — Crude **2**, prepared from **1** (60 g) without subsequent chromatographic purification, was dissolved in glacial acetic acid (850 ml), treated with sulfuric acid (3 ml) in water (400 ml), and heated for 2 h on a steam bath. T.l.c. (9:1 ethyl acetate–methanol, 1 ascent or ethyl acetate, 2 ascents) showed approximately equal amounts of **9** and an unknown component of higher R_F value that did not align with **2** or **3**. The hydrolyzate was treated with sodium hydrogen carbonate (12 g), evaporated, and then extracted with hexane. The extract was discarded, and the insoluble mixture of salts and products was then extracted with warm acetone to remove **9** and the unknown component. The extract was coated on silica gel (100 g) by evaporation, and the final powder was packed into a partially filled column of silica gel (400 g) in ethyl acetate. Elution with ethyl acetate removed the unknown product, obtained as a syrup (16 g) soluble in chloroform or ether. Subsequent elution of the column with 17:3 ethyl acetate–methanol yielded **9** (27 g, 57%), also a syrup but insoluble in chloroform or ether.

1,2,4,6-Tetra-O-acetyl-3-O-benzyl-β-D-allose (**10**). — A 5-g portion of **9** was kept for 48 h at 25° in 1:1 acetic acid–pyridine (20 ml), evaporated at 60°, and then purified by preparative t.l.c. (chloroform). Distillation of the purified extract (230°/0.1 mtorr) gave **10** (7.6 g); $[\alpha]_{546}^{27}$ −2.7° (*c* 4.6, chloroform).

Anal. Calc. for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.52; H, 6.09.

Acetylation of the unknown component, either as described for **9** or with acetic anhydride–sodium acetate (10:1, v/w) at 100° with subsequent purification, yielded pure **10**.

Condensation of acetaldehyde with **9**. — *A*. After gentle shaking for 3 days at 25°, a mixture of **9** (14 g), paraldehyde (10 ml), and sulfuric acid (0.2 g) afforded a mass of crystals and syrup, which was dispersed in ether (100 ml) and filtered. Each fraction was treated separately with 1-ml portions of ammonium hydroxide and stored at −5° for later processing.

B. Paraldehyde (5 ml) and sulfuric acid (0.7 g) were added to a solution of **9** (27 g) in methyl sulfoxide (10 ml) and the mixture was kept for 48 h at 45°. The solution was diluted with chloroform (100 ml), stirred for 1 h with sodium hydrogen carbonate (5 g), and then filtered. Solids were washed on a funnel with small volumes of methanol (4–5 ml) and discarded. The combined filtrates were evaporated (85°), taken up in ethyl acetate, refiltered, and then compared by t.l.c. to the fractions from *A* (4:1 benzene–ether, 2 ascents; 9:1 ethyl acetate–methanol; 9:1 chloroform–acetone). Three major groups of products were detected in *A* and *B*: **11**, **12**; **15**, **16**, and **17**; and two unknowns more mobile than **15**, **16**, and **17** but less mobile than **11** or **12**.

3-O-Benzyl-1,2:5,6-di-O-ethylidene-α-D-alloses (**11**, **12**). — The ether-soluble fraction from *A* was chromatographed on a silica gel column packed and eluted with benzene, until highly mobile by-products had been washed off, and then with 9:1 benzene–ethyl acetate to obtain three fractions: pure **11** (1.9 g), a fraction rich in **12** (3.2 g), and the unknown components. Elution with ethyl acetate afforded another fraction (4.3 g) that contained **15**, **16**, and **17** (t.l.c., 7:3 ether–ethyl acetate, 2 ascents). Recrystallization of **11** from heptane gave pure material: m.p. 82.5–83°, $[\alpha]_{546}^{25}$ +132.6° (*c* 1.1, chloroform).

Anal. Calc. for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.22; H, 6.98.

Crystallization from heptane after refractionation (4:1 benzene–ether, 2 ascents) produced pure 12; m.p. 69–71°, $[\alpha]_{546}^{25}$ +147.3° (*c* 0.53, chloroform). The purity exceeded 95%, as judged by g.l.c. (225°).

Anal. Calc. for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.02; H, 6.83.

3-O-Benzyl-4,6-O-ethylidene-β-D-allose (**17**). — Fractionation of mixture *B* on a silica gel column with 1:1 ethyl acetate–ether gave **17** (4.4 g), a mixed fraction (13.8 g) from which additional **17** (2.6 g) was isolated by fractional crystallization (acetone, ether, and then hexane–ether), and a fraction (3.4 g) containing **11**, **12**, and the unknown products. Crystalline **17** from *B* was combined with the original solids from *A* (3 g) and recrystallized from aqueous ethanol; m.p. 158–160°, $[\alpha]_{546}^{27}$ −38.9°→ −31.6° (*c* 1, 72 h in methanol).

Anal. Calc. for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.52; H, 6.72.

Refractionation of the noncrystalline residue containing **15**, **16**, and **17** by preparative t.l.c. (4:1 benzene–ether, 2 ascents) after a preliminary acetylation yielded **5** and **6**, as judged by n.m.r. spectroscopy.

1,2-Di-O-acetyl-3-O-benzyl-4,6-O-ethylidene-β-D-allose (**18**). — Acetylation of **17** (2 g) in 1:1 acetic anhydride–pyridine (8 ml) for 24 h at −5° and then for another 24 h at 25° gave a crystalline residue after evaporation of volatiles. Recrystallization from ethanol gave pure **18**; m.p. 103–104°, $[\alpha]_{546}^{27}$ −116.3° (*c* 1.4, chloroform).

Anal. Calc. for $C_{19}H_{24}O_8$: C, 59.99; H, 6.36. Found: 59.75; H, 6.29.

Formation of **5** *from* **11**, **12**. — A 0.4-g mixture of **11** and **12** (1:1) was dissolved in aqueous acetic acid (1:3, 4 ml), heated for 40 min at 100°, and then evaporated. The residue was kept for 48 h at 25° in 1:1 acetic anhydride–pyridine, 4 ml) with subsequent evaporation of volatiles. Pure **5** (0.33 g) was isolated by preparative t.l.c. (4:1 benzene–ether, 1 ascent). Isomerization of the sample by keeping it for 3 h at 25° in chloroform-*d* saturated with anhydrous hydrogen chloride increased the content of **6** from trace levels to 18%, as judged by n.m.r. spectroscopy.

Cleavage of benzyl ethers. — *A*. A 1:1 mixture of **11** and **12** (1.2 g) in anhydrous methanol (200 ml) was treated with 10% palladium on powdered charcoal (1.6 g, Matheson, Coleman & Bell) and then shaken under hydrogen (40 lb.in.$^{-2}$) for 8 h at 25°. Reduction was complete (t.l.c., chloroform, 2 ascents; 9:1 chloroform–acetone), with formation of a small amount of a mono-*O*-ethylidene product. The syrupy mixture (0.8 g) was acetylated at −5°, and the diastereoisomeric **13** and **14** were separated partially by preparative t.l.c. (7:3 benzene–ether, 2 ascents). Neither isomer was more than 90% pure after distillation (180°/0.1 mtorr), and each contained small proportions of **7**. The purity was sufficient to establish the structures by n.m.r. spectroscopy. G.l.c. separation of **13** and **14** (160°) was incomplete because of partial peak overlap, a condition not observed for the 3-hydroxyl analogs (170°, unsilylated sample).

B. For **5**, a 1.1-g sample was treated as described for *A*, acetylated, and similarly isolated. The ratio of **7**:**8** was estimated to be 9:1 by n.m.r. Samples from *A* and *B* were not examined further.

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