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SYNTHESIS OF BRANCHED-CHAIN SUGAR DERIVATIVES RELATED TO ALDGAROSE*

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ABSTRACT

Ethynylation of 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**1**) gave the 3-*C*-ethynyl *allo* derivative **2**, together with an adduct (**3**) resulting from interaction of two molecules of **1** with one of acetylene. Lithium aluminum hydride reduced the acetylenes **2** and **3** to the corresponding alkenes **4** and **8**; on sequential ozonolysis–borohydride reduction, these both gave 3-*C*-(hydroxymethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**6**), further characterized as its $3,3^1$-cyclic carbonate **9**. Ozonolysis of the acetylene **2** gave the $3^1,5$-lactone (**5**) of the 3-*C*-carboxy analog, thus establishing the stereochemistry of **2**, which was independently established by n.m.r. spectroscopy employing a lanthanide shift-reagent. Treatment of **2** with mercuric acetate in ethyl acetate, followed by hydrogen sulfide, gave a mixture of the 3-*C*-acetyl-3-*O*-acetyl derivative **10** and a product (**11**) derived from internal cyclization of 5,6-deacetonated, *O*-deacetylated **10**. Reduction of **10** with lithium aluminum hydride gave a separable mixture of diastereoisomeric 3-*C*-(1-hydroxyethyl) derivatives (**12a, 12b**) that were individually converted into their corresponding $3,3^1$-cyclic carbonates **13a** and **13b**, products that contain the branch functionality of the unusual, branched-chain sugar aldgarose.

INTRODUCTION

For synthesis of sugars of unusual functionality, such as are frequently encountered in carbohydrate antibiotics, chain-extension and chain-branching reactions based on addition of ethynylmagnesium bromide and other unsaturated Grignard reagents to aldehydo and keto sugars have been found of wide utility, as exemplified by earlier papers in this series[1,3,4]. This report demonstrates the use of the ethynylation approach for introducing a *C*-(1-hydroxyethyl) chain-branch into a sugar and

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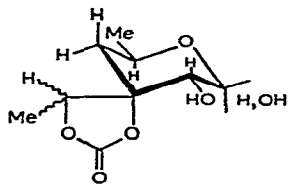
converting it into a spiro carbonate derivative, to afford, in high net yield, the chain-branch functionality of aldgarose. Aldgarose is[5] a constituent of the antibiotic aldgamycin E; syntheses of it[6] and related analogs[7] by way of dithianyl anions have



Aldgarose

been reported. The present syntheses also provide a convenient route to 3-*C*-(hydroxymethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**6**); a deacetonated 5-carboxy pentose analog of this product has been postulated[8] as a constituent of a bilirubin conjugate found in human bile. The syntheses are also of potential utility in routes to other branched-chain sugars, such as the 4-*C*-(1-hydroxyethyl)[9,10] and 4-*C*-acetyl[10] sugars identified in the quinocycline complex of antibiotics.

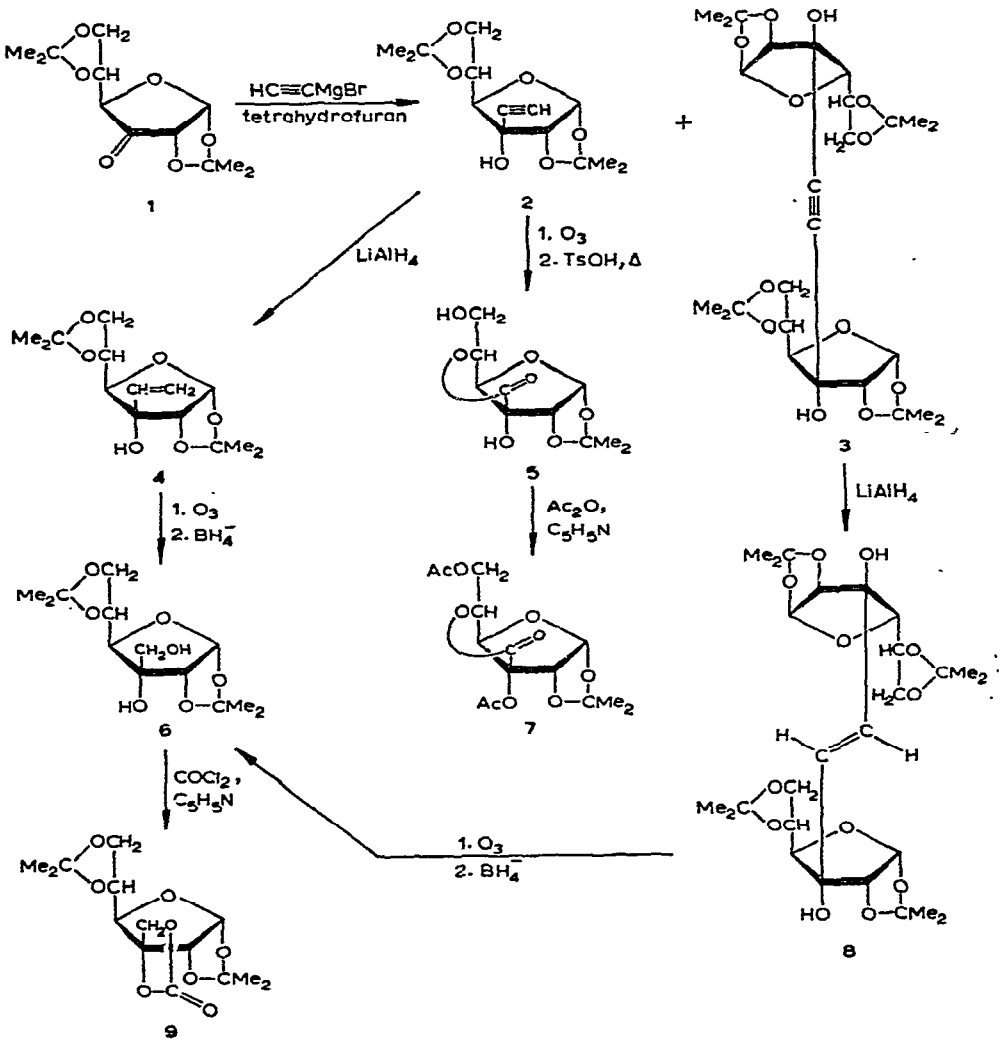
DISCUSSION

The chain-branching step in this synthesis was achieved by ethynylation[4,11–13] of the readily available 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose[14] (**1**, prepared by dehydration of the hydrate from a large-scale preparation[15]). A single product was obtained in 86% yield; the stereospecificity of the reaction was verified by g.l.c., t.l.c., and n.m.r.-spectral analysis, and the product was formulated as the D-*allo* adduct **2** on the basis of the general stereochemical control observed[14–16] in nucleophilic addition-reactions to **1**.

The D-*allo* configuration was firmly established for the product **2** by ozonolysis and subsequent mild treatment with acid to afford a crystalline lactone formulated as **5**, arising through successive conversion of the 3-*C*-ethynyl group into a carboxyl group, removal of the 5,6-*O*-isopropylidene group, and lactone formation between O-5 and the carboxyl group. This lactone can be formed from the D-*allo* precursor **2**, but not from its 3-epimer. Structure **5** was established for the lactone from its molecular formula, from its n.m.r. spectrum* (which was first-order, indicated that the 1,2-*O*-isopropylidenetetrofuranose moiety was present, and showed other signals concordant with the assigned structure) and by i.r. spectroscopy, which showed a carbonyl-stretching absorption at 5.68 μm in the range diagnostic for a 5-membered lactone ring. In comparison, a known[17] 6-membered-ring lactone [3-*C*-(carboxymethyl)-1,2-*O*-isopropylidene-α-D-allofuranose-3^2,5-lactone] of related structure shows carbonyl-group absorption at distinctly longer wavelength (5.76 μm). Further-

*Details of n.m.r. and mass spectra are recorded in Tables I and II, respectively, given at the end of the Discussion section.

more, acetylation of **5** gave a crystalline diacetate **7** in which the H-6,6′ signals resonated ~0.6 p.p.m. to lower field than in **5**, whereas the H-5 signal showed very little displacement; this result indicated that the parent lactone has a free hydroxyl group at C-6 and that O-5 is engaged in the lactone ring.



An independent confirmation of the stereochemistry of **2** was afforded by observing the effects of incremental addition of the lanthanide shift-reagent[18] tris-[1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato]europium(III), [Eu(fod)$_3$], on the n.m.r. spectrum of **2** (see Fig. 1). This technique has been utilized in this laboratory[19] for assigning stereochemistry to the tertiary alcoholic group of similar ethynylated adducts and other branched-chain sugar derivatives[20]; when suitable

reference-compounds are available, an unambiguous stereochemical assignment can be made. The shift-reagent interacts with **2** to cause marked downfield shifts of H-2 and H-4, whereas the downfield shift-gradient for H-5 is relatively small. This behavior indicates interaction of the shift-reagent with the 3-OH group on the "under" side of the molecule of **2**; it is exactly analogous to the behavior observed[21] with 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose, and is in sharp contrast to the behavior with 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, where the shift-reagent coordinates with the 3-OH group on the "top" side of the molecule, and H-5 exhibits a marked downfield shift-gradient.

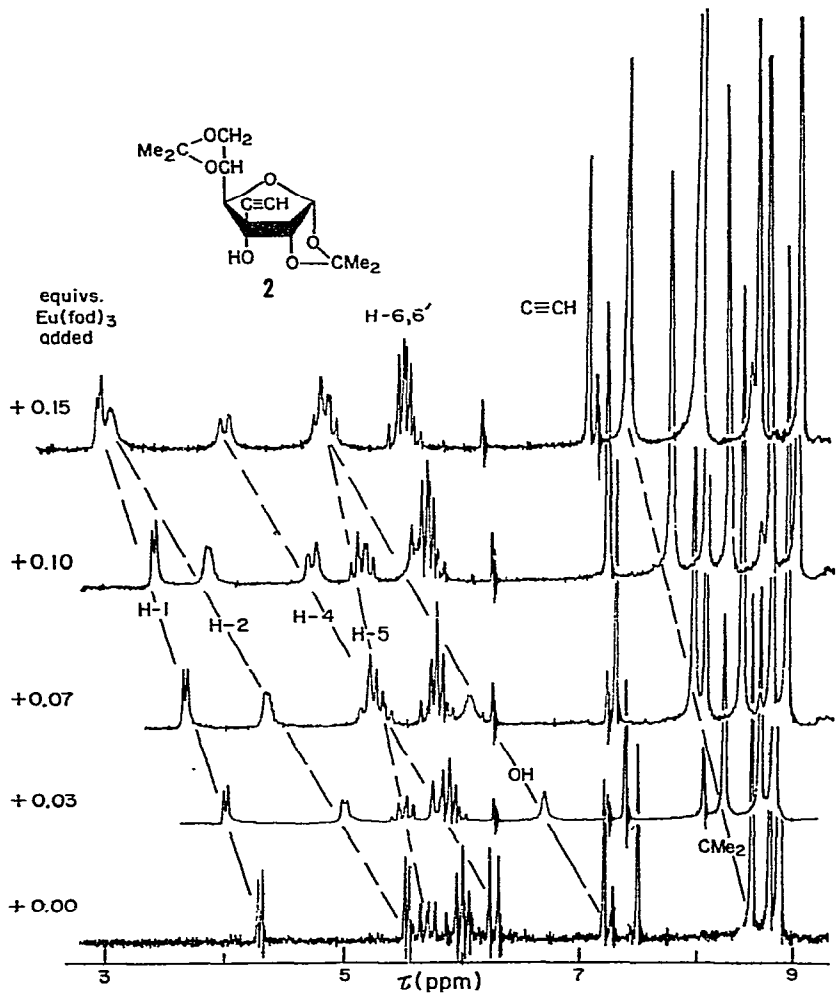


Fig. 1. The 100-MHz n.m.r. spectrum of **2** in chloroform at ~30° in the presence of the indicated number of equivalents of tris[1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato]europium(III), [Eu(fod)$_3$].

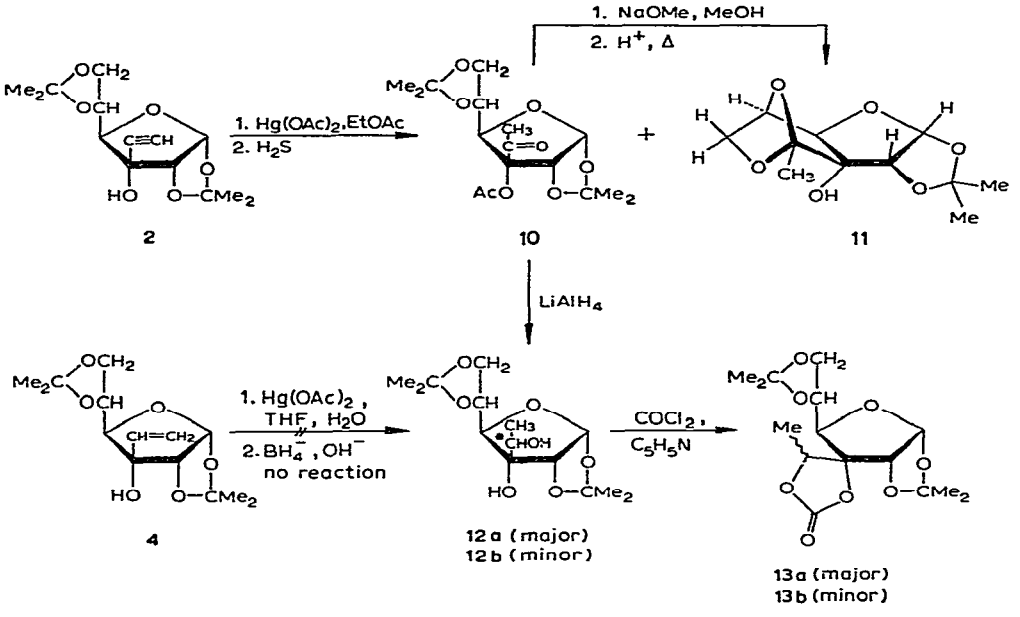
When the intial reaction-mixture for the Grignard reaction with **1** was not fully saturated with acetylene, a by-product, amounting to 25–30% of the total product, was formed, and it was isolated crystalline by column chromatography on silica gel. The great similarity of the n.m.r. spectrum of this by-product to that of the major product **2** (except for the absence of the acetylenic-proton signal), together with the mass of its $M^{+} - \cdot CH_3$ ion (*m/e* 527.2137 daltons; calc. for $C_{25}H_{35}O_{12}$, 527.2128 daltons), led to assignment of the symmetrical structure 1,2-bis(1,2:5,6-di-*O*-isopropylidene-α-D-allofuranos-3-yl)acetylene (**3**) to the by-product. This formulation was supported by an acceptable elemental analysis and the absence of acetylenic C–H or C≡C absorptions in the i.r. spectrum. Direct ozonolysis–acid treatment of **3** gave the lactone **5**, but only in low yield, as determined by t.l.c. However, reduction of **3** with lithium aluminum hydride gave, in almost quantitative yield, the corresponding alkene **8**. Because of the symmetry of this molecule, the alkenic protons gave rise to a singlet n.m.r. signal, so that the vicinal H–C=C–H coupling could not be observed; the *trans* configuration is presumed from the known[22] steric course of such reductions. Ozonolysis of the alkene **8**, and borohydride reduction of the product, afforded crystalline 3-*C*-(hydroxymethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**6**) in good yield. This product was identical with the product of sequential ozonolysis–reduction of 1,2:5,6-di-*O*-isopropylidene-3-*C*-vinyl-α-D-allofuranose (**4**, see next paragraph), thus furnishing firm structural evidence for **3** and its reduction product **4**.

Reduction of the acetylene **2** with lithium aluminum hydride gave the corresponding, crystalline 3-*C*-vinyl analog **4** in 79% yield. This same compound could be obtained in one step from the ketone **1** by reaction with vinylmagnesium chloride, but the yield was low; the two-step route of ethynylation of **1** followed by reduction constituted the better preparative route to **4**. The two-step route has been found superior to direct vinylation in other syntheses of this type[23].

Ozonolysis of the 3-*C*-vinyl derivative **4** and borohydride reduction of the product gave 84% of crystalline 3-*C*-(hydroxymethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**6**). This product differed from the known[17,24] D-*gluco* epimer; it gave acceptable elemental analyses, and its mass spectrum was in accord with the structure assigned. The n.m.r. spectrum showed two exchangeable protons, and correct integrals for the remaining protons; the H-3[1],4,5,6 resonances gave rise to a series of complex, overlapping signals. Treatment of **6** with phosgene in pyridine gave 73% of the (crystalline) cyclic carbonate **9**, m.p. 116–116.5°, $[\alpha]_D$ +40° (chloroform), clearly different from the known[24] D-*gluco* analog, which has been reported as an oil having $[\alpha]_D$ +16° (chloroform). The ring-proton resonances of **9** were not entirely resolved, but a broad, two-proton signal at τ 6.12 could be attributed to protons of the chain-branch methylene group, resonating at lower field than for the parent diol **6**. The i.r. spectrum of **9** showed strong carbonyl absorption at 5.42 and 5.50 μm, indicative[5,17,24] of a *spiro* cyclic carbonate structure.

To generate the desired 3-*C*-(1-hydroxyethyl) chain branch *via* an intermediate 3-*C*-acetyl derivative, the acetylene **2** was subjected to a modification[25] of a mild, relatively non-acidic, hydration procedure[26,27] that employs mercury(II) acetate in a

medium of ethyl acetate. The reaction at room temperature was slow, but chromatographic resolution of the product after 14 days gave two new products, 38% of 3-*C*-acetyl-3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**10**) as an oil, and 39% of crystalline 1,2-*O*-isopropylidene-[3-*C*,5-*O*,6-*O*-(methylmethylidyne)]-α-D-allofuranose (**11**), together with 14% of recovered acetylene **2**.



Spectral data provided clear confirmation of the structure **10**. The i.r. spectrum showed two absorptions (at 5.71 and 5.82 μm) in the carbonyl region, and hydroxyl-group absorption was absent. The molecular formula of $C_{16}H_{24}O_8$ was indicated by the elemental analysis and by the appearance of an $M^{+} - \cdot CH_3$ fragment in the mass spectrum; other mass-spectral fragments also supported structure **10**. The n.m.r. spectrum showed, in addition to the signals for the two isopropylidene groups, two methyl-group signals as singlets (τ 7.75 and 7.82 in chloroform-*d*), in accord with the presence of a *C*-acetyl and an *O*-acetyl group. Thus, it is evident that the hydration procedure led to concurrent acetylation of the tertiary hydroxyl group; none of the non-*O*-acetylated analog of **10** could be detected by g.l.c.–mass spectrometry of the crude reaction-mixture. A similar acylation has been recorded in the steroid literature, wherein a sterically accessible, tertiary hydroxyl group became acetylated during the course of a mercury(II)-mediated hydration of a propargylic alcohol; a cyclic mechanism involving a mercury complex has been proposed[25].

The crystalline product formulated as **11**, isolated in a yield comparable to that of **10** from the hydration reaction, displayed hydroxyl-stretching absorption at 2.88 μm in its i.r. spectrum, and carbonyl-group absorption was absent. The n.m.r. spectrum indicated that only one isopropylidene group remained in the product; there was an

additional *C*-methyl resonance in the $\tau \sim 8.5$ region, and one exchangeable proton was present. The elemental analysis and the mass spectrum (*m/e* 244.0949 daltons for $M^{+\cdot}$) accorded with the molecular formula $C_{11}H_{16}O_6$ (*m/e* calc., 244.0947 daltons). Further evidence for the assigned structure was provided by conversion of the ketone **10** into compound **11**. *O*-Deacetylation of **10** required severe conditions (boiling, methanolic sodium methoxide), but the product was evidently the anticipated 3-hydroxy analog of **10**, as it gave at highest mass an ion having *m/e* 287 (16% intensity, assigned to $M^{+\cdot} - \cdot CH_3$) and an ion at *m/e* 101 (100%, base peak) that can be attributed to the $C_5H_9O_2^+$ fragment typical[28] of 5,6-*O*-isopropylidenealdohexofuranoses. Treatment of the *O*-deacetylated product with dilute acetic acid to cleave the 5,6-*O*-isopropylidene group, followed by heating in ethanol to effect dehydration, gave a mixture of products. One of these, approximately one-third of the total reaction-mixture, was indistinguishable from **11** by t.l.c. and g.l.c., and its mass spectrum was identical to that of compound **11**.

It is noteworthy that, in contrast to compound **10**, the product **11** is not acetylated at O-3, and none of the 3-*O*-acetylated analog of **11** could be detected by g.l.c.–mass spectrometry of the crude reaction mixture obtained on hydration of **2**. Presumably, **11** is formed through deacetonation at O-5 and O-6 of a precursor, and formation of the intramolecular acetal. It remains unclear whether the reaction sequence is simply an acid-mediated process, or whether a mercury–acetylene complex (a system known[29] to catalyze acetal formation) is involved. The mercury(II) acetate–ethyl acetate system, although of demonstrated mildness and usefulness in the presence of cyclic acetals[25], is not entirely non-acidic, as shown by the stoichiometry of the process[26]. However, as rather vigorous conditions were required to convert **10** into **11**, and a relatively low yield of **11** was obtained, it is suggested that an orderly, energetically favored process, probably through an organo-mercury intermediate, is involved, and that this accounts for the almost 1:1 ratio of the products **10** and **11** obtained upon hydration of **2**.

Attempts to oxymercurate the 3-*C*-vinyl derivative **4** by the procedure of Brown and Geoghegan[30] failed, despite numerous variations of the reaction conditions; starting material was invariably recovered. Evidently, this 3-*C*-substituent is sufficiently hindered sterically to inhibit formation and reaction of an organo-mercury complex.

For the reductive step to generate the 3-*C*-(1-hydroxyethyl) derivative from the 3-*C*-acetyl precursor **10**, the relative merits of sodium borohydride, sodium bis(2-methoxyethoxy)aluminum hydride, and lithium aluminum hydride were evaluated as reductants; the last-named reagent proved the most satisfactory. Prolonged treatment of **10** with lithium aluminum hydride in refluxing tetrahydrofuran was needed to effect complete reduction of the carbonyl group with concomitant cleavage of the *O*-acetyl group, but the reaction afforded the 3^1-epimeric diols **12a** and **12b** in almost quantitative yield as a 2:1 mixture. The epimers were readily separated by t.l.c. or by column chromatography on silica gel, and both were obtained as crystalline, sharp-melting, single products. Their specific optical rotations differed by only 12.5° and

TABLE I

N.M.R. SPECTRAL DATA[a] FOR COMPOUNDS 2–13

Compound	*Solvent*	*Chemical shifts in τ values (first-order couplings in parentheses)*						
		H-1	*H-2*	*H-4*	*H-5*	*H-6,6'*	*C(Me)₂*	*Other*
3-*C*-Ethynyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (2)[b]	$CDCl_3$	4.34 d ($J_{1,2}$ 3.7)	5.57 d	6.29 d ($J_{4,5}$ 7.1)	5.71 m (width 19.5 Hz)	5.95, 6.08 m[c] ($J_{6,6'}$ 8.7, $J_{3,6}$ 8.1, $J_{5,6'}$ 3.1)	8.45, 8.59, 8.66, 8.69	7.20 s[d] (O*H*); 7.48 s, (acetylenic)
Bis(1,2:5,6-di-*O*-isopropylidene-α-D-allofuranos-3-yl)acetylene (3)[e]	$CDCl_3$	4.25 d ($J_{1,2}$ 3.4)	5.43 d	6.18 d ($J_{4,5}$ 8)	5.66 m (width 17.5 Hz)	6.0 m (width 24 Hz)	8.42, 8.55, 8.74 (6*H*)	6.82 s[d] (O*H*)
1,2:5,6-Di-*O*-isopropylidene-3-*C*-vinyl-α-D-allofuranose (4)	$CDCl_3$	4.27 d ($J_{1,2}$ 3.9)	5.76 d	5.87———		———6.72 m	8.40, 8.58, 8.66, 8.69 (s)	7.20 s[d] (O*H*) 4.13 dd H-3[1] (J_{cis} 10.0, J_{trans} 17.1); 4.45 dd, 4.65 dd, H-3[2], H-3[2a] (J_{gem} 2.5)
3-*C*-Carboxy-1,2-*O*-isopropylidene-α-D-allofuranose-3[1],5-lactone (5)	$(CD_3)_2CO$	4.12 d ($J_{1,2}$ 4.0)	5.36 d	5.49 s ($J_{4,5}$ ≈0)	5.54 t[f]	6.17 d[f] ($J_{5,6}$ ~6)	8.48, 8.65	6.95 s[d] (O*H*, 2 protons)
3-*C*-(Hydroxymethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (6)	C_6D_6[g]	4.51 d ($J_{1,2}$ 3.7)	5.61 d	5.8———		———7.0 m[h]	8.60, 8.65, 8.77, 8.90,	7.2 s[d] (O*H*)
	$CDCl_3$	4.25 d	5.44 d	5.79———		———6.4 m[h]	8.41, 8.53, 8.63	5.66 d[d] (O*H*) 6.67 s[d] (O*H*)
3,6-Di-*O*-acetyl-3-*C*-carboxy-1,2-*O*-isopropylidene-α-D-allofuranose-3[1],5-lactone (7)	$(CD_3)_2CO$	3.92 d ($J_{1,2}$ 3.8)	4.98 d	5.06 d ($J_{4,5}$ 2.0)	5.36 m[h] (width 14 Hz)	5.61 s, 5.66 d[g] ($J_{5,6}$ 6.5)	8.37, 8.60	7.84, 7.94 (OAc)
trans-1,2-Bis(1,2:5,6-di-*O*-isopropylidene-α-D-allofuranos-3-yl)ethylene (8)	$CDCl_3$	4.22 d ($J_{1,2}$ 3.6)	5.76 d	5.82———		———6.16 m	8.38, 8.56, 8.64, 8.67	7.13 s[d] (O*H*), 4.02 s (vinyl)

TABLE I (*continued*)

Compound	*Solvent*	*Chemical shifts in τ values (first-order couplings in parentheses)*						
		H-1	*H-2*	*H-4*	*H-5*	*H-6,6'*	*C(Me)₂*	*Other*
3,3¹-*O*-Carbonyl-3-*C*-(hydroxymethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**9**)	C_6D_6	4.82 d ($J_{1,2}$ 3.8)	5.79 d	6.53 d ($J_{4,5}$ 9.1)	5.8 m	6.06—6.25 m[h]	8.49 (6*H*), 8.76, 8.79	
3-*C*-Acetyl-3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**10**)	$CDCl_3$	4.17 d ($J_{1,2}$ 4.0)	5.01 d	5.82———		———6.26 m	8.48, 8.52, 8.67 (6*H*)	7.75 s (*C*-Ac), 7.82 s (*O*-Ac)
1,2-*O*-Isopropylidene-[3-*C*,5-*O*,6-*O*-(methyl methylidyne)]-α-D-allofuranose (**11**)	$CDCl_3$	4.14 d ($J_{1,2}$ 4.0)	5.67 d	5.83 s ($J_{4,5}$ ≈0)	5.51 t ($J_{5,6}$ 4.5)	6.31 d, 6.37 s[g]		6.79 s[d] (O*H*); 8.42 (6*H*); 8.57 (3*H*)
3-*C*-(1¹-Hydroxyethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**12a**)	$CDCl_3$	4.29 d ($J_{1,2}$ 4.1)	5.46 d	5.70———		———6.20 m	8.41, 8.45, 8.63 (6*H*)	5.90 q, H-3¹ ($J_{3^1,3^2}$ 7); 6.9 s[d] (O*H*); 8.83 d, H-3²
3-*C*-(1¹-Hydroxyethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**12b**)	$CDCl_3$	4.22 d ($J_{1,2}$ 4.2)	5.48 d	6.08 d ($J_{4,5}$ 6.0)	4.2 m ($J_{5,6}$ 6.5)	5.91 d[f]	8.41, 8.49, 8.59 (6*H*)	5.71 q, H-3¹ ($J_{3^1,3^2}$ 6.2); 7.07 s[d] (O*H*); 8.69 d, H-3²
3,3¹-*O*-Carbonyl-3-*C*-(1¹-hydroxyethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**13a**)	$CDCl_3$	4.36 d ($J_{1,2}$ 3.5)	5.31 d	5.14———		———6.2 m	8.39, 8.50, 8.56, 8.62, 8.67[j]	5.01 q, H-3¹ ($J_{3^1,3^2}$ 6.5)
3,3¹-*O*-Carbonyl-3-*C*-(1¹-hydroxyethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**13b**)	$CDCl_3$	4.24 d ($J_{1,2}$ 3.5)	5.56 d	5.83 m	5.53 m ($J_{5,6}$ 4)	5.86, 6.11 m[f]	8.30, 8.37, 8.38, 8.54, 8.63, 8.67	5.28 q, H-3¹ ($J_{3^1,3^2}$ 6.2)

[a]Apparent first-order couplings are given in Hz; peak multiplicities: d, doublet; dd, doublet of doublets; q, quartet; s, singlet; t, triplet. [b]For spectrum with $Eu(fod)_3$ added, see Fig. 1. [c]An AB portion of ABX system; calculated couplings and chemical shifts are given. [d]Exchanges upon addition of D_2O. [e]Spectrum at 60 MHz. [f]Apparent A_2X pattern. [g]AB portion of ABX system that approaches A_2X; outer transitions undetectable. [h]Includes H-3¹,3¹ᵃ. [i]A 7-line symmetrical multiplet. [j]$C(Me)_2$ and 3²-Me resonances not distinguished.

TABLE II

MASS-SPECTRAL DATA FOR COMPOUNDS 2–13

Compound	*Mass-spectral peaks (relative intensities and probable assignments are given in parentheses)*
3-*C*-Ethynyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (2)	269 (37) ($M^+ - CH_3\cdot$), 243 (1) ($269 - C_2H_2$), 226 (<1) ($M^+ - C_3H_6O$), 211 (1) ($226 - CH_3\cdot$), 189 (3), 183 (<1) ($M^+ - C_5H_9O_2$), 168 (7) ($183 - CH_3\cdot$), 153 (4) ($M^+ - C_6H_{11}O_3$), 151 (5) ($C_8H_7O_3^+$), 138 (4) ($153 - CH_3\cdot$), 131 (41) ($M^+ - C_8H_9O_3$), 123 (8) ($C_7H_7O_2$), 113 (3), 111 (4), 110 (11), 109 (5), 101 (36) ($C_5H_9O_2^+$), 97 (11) ($C_5H_5O_2^+$), 96 (13), 95 (4), 93 (7), 85 (9) ($C_4H_5O_2^+$), 73 (4), 72 (19), 71 (6) ($C_3H_3O_2$), 68 (5), (65) (7), 59 (78) ($C_3H_7O^+$), 43 (100) ($C_2H_3O^+$)
1,2-Bis-(1,2:5,6-di-*O*-isopropylidene-α-D-allofuranos-3-yl)-acetylene (3)	527 (50) ($M^+ - CH_3\cdot$), 469 (1) ($527 - C_3H_6O$), 441 (<1) ($M^+ - C_5H_9O_2$,) 426 (1) ($441 - CH_3\cdot$), 411 (1) ($426 - CH_3\cdot$), 383 (1) ($441 - C_3H_6O$), 366 (1) ($426 - CH_3CO_2H$), 365 (1), 353 (4) ($411 - C_3H_6O$), 352 (3), 339 (2), 337 (2), 312 (2), 297 (5), 296 (6), 293 (3), 281 (2), 269 (2), 265 (2), 256 (3), 253 (4), 238 (5), 221 (4), 208 (7), 193 (7), 182 (10), 166 (10), 137 (10), 131 (29), 101 (83) ($C_5H_9O_2^+$), 85 (24) ($C_4H_5O_2^+$), 72 (22), 59 (45) ($C_3H_7O^+$), 43 (100) ($C_2H_3O^+$)
1,2:5,6-Di-*O*-isopropylidene-3-*C*-vinyl-α-D-allofuranose (4)	286 (<1) (M^+), 271 (23) ($M^+ - CH_3\cdot$), 228 (2) ($M^+ - C_2H_6O$), 213 (1) ($271 - C_3H_6O$), 189 (2), 185 (1) ($M^+ - C_5H_9O_2\cdot$), 171 (4), 170 (9) ($185 - CH_3\cdot$), 153 (6) ($C_8H_9O_3$), 127 (1) ($C_6H_7O_3$), 125 (4) ($C_7H_9O_2$), 98 (67), 99 (36) ($C_5H_5O_2$), 95 (10), 85 (9) ($101 - CH_3\cdot - H\cdot$), 72 (21), 59 (75) ($C_3H_7O^+$), 55 (50)(C_3H_3O), 43 (100) (C_2H_3O)
3-*C*-Carboxy-1,2-*O*-isopropylidene-α-D-allofuranose-3^1,5-lactone (5)	231 (22) ($M^+ - CH_3\cdot$), 188 (9) ($M^+ - C_3H_6O$), 171 (28) ($231 - CH_3CO_2H$), 158 (12), 153 (10) ($171 - H_2O$), 125 (3) ($153 - CO$), 141 (6), 130 (9), 113 (5), 101 (7) ($C_5H_9O_2^+$), 100 (30) ($C_4H_4O_3^+$), 89 (5), 85 (14) ($101 - CH_3\cdot - H\cdot$), 71 (12), 59 (90) ($C_3H_7O^+$), 43 (100) ($C_2H_3O^+$)
3-*C*-(Hydroxymethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (6)	275 (40) ($M^+ - CH_3\cdot$), 257 (2) ($275 - H_2O$), 233 (1), 217 (10) ($275 - C_3H_6O$), 215 (3) ($275 - C_2H_4O_2$), 201 (2), 199 (2), 189 (5) ($M^+ - C_5H_9O_2\cdot$), 175 (3), 174 (1), 172 (3), 171 (1) ($189 - H_2O$), 159 (4), 158 (1) ($189 - \cdot CH_2OH$), 157 (12) ($215 - C_3H_6O$), 143 (10), 139 (15) ($C_7H_7O_3$), 131 (18) ($189 - C_3H_6O$), 129 (4), 126 (4) ($157 - \cdot CH_2OH$), 116 (8), 113 (14) ($C_5H_5O_3$), 101 (72) ($C_5H_9O_2^+$), 100 (16) ($C_4H_4O_3^+$), 99 (10), 85 (26) ($C_4H_5O_2$), 72 (22), 59 (79) ($C_3H_7O^+$), 57 (10), 43 (100) ($C_2H_3O^+$)
3,6-Di-*O*-acetyl-3-*C*-carboxy-1,2-*O*-isopropylidene-α-D-allofuranose-3^1,5-lactone (7)	315 (32) ($M^+ - CH_3\cdot$), 288 (3) ($MH^+ - C_2H_3O$), 273 (1) ($288 - CH_3\cdot$), 257 (<1) ($C_{11}H_{13}O_7^+$), 255 (<1) ($315 - CH_3CO_2H$), 241 (1), 231 (1), 214 (14), 196 (8), 171 (12), 153 (21) ($171 - H_2O$), 142 (4), 125 (9) ($153 - CO$), 113 (2), 101 (3), 100 (2) ($C_4H_4O_3^+$), 85 (5), 71 (3), 59 (8) ($C_3H_7O^+$), 43 (100) ($C_2H_3O^+$)
trans-1,2-Bis(1,2:5,6-di-*O*-isopropylidene-α-D-allofuranos-3-yl)ethylene (8)	529 (55) ($M^+ - CH_3\cdot$), 428 (1) ($529 - C_5H_9O_2\cdot$), 425 (2), 413 (1) ($428 - CH_3\cdot$), 411 (2), 370 (1) ($428 - C_3H_6O$), 355 (8) ($413 - C_3H_6O$), 353 (2), 337 (3), 312 (4), 298 (15), 256 (6), 240 (12), 211 (7), 197 (10), 182 (7), 168 (24), 131 (18), 101 (65) ($C_5H_9O_2^+$), 100 (95) ($C_4H_4O_3^+$), 97 (22), 85 (25) ($C_4H_5O_2^+$), 71 (16), 59 (40) ($C_3H_7O^+$), 43 (100) ($C_2H_3O^+$)

TABLE II (*continued*)

Compound	*Mass-spectral peaks (relative intensities and probable assignments are given in parentheses)*
3,3^1-*O*-Carbonyl-3-*C*-(hydroxymethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**9**)	301 (100) ($M^+ - CH_3\cdot$), 288 (11) ($M^+ - 28$), 269 (10) ($301 - CH_4O$), 243 (5) ($301 - C_3H_6O$), 241 (4) ($301 - CH_3CO_2H$), 201 (2), 200 (3) ($301 - C_5H_9O_2\cdot$), 187 (8) ($288 - C_5H_9O_2\cdot$), 183 (20) ($241 - C_3H_6O$), 149 (9), 143 (5), 139 (15), 129 (14), 115 (5), 111 (7), 101 (98) ($C_5H_9O_2^+$), 97 (6), 85 (11) ($C_4H_5O_2^+$), 83 (10), 81 (8), 72 (44), 59 (22) ($C_3H_7O^+$), 57 (14), 55 (36), 43 (98) ($C_2H_3O^+$)
3-*C*-Acetyl-3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**10**)	329 (3) ($M^+ - CH_3\cdot$), 271 (4) ($329 - C_3H_6O$), 243 (3) ($M^+ - C_5H_9O_2\cdot$), 228 (1) ($243 - CH_3\cdot$), 211 (1) ($271 - CH_3CO_2H$), 185 (11) ($228 - C_2H_3O$), 155 (4), 153 (8), 151 (1) ($211 - CH_3CO_2H$), 143 (6), 141 (4), 127 (7), 101 (69) ($C_5H_9O_2^+$), 97 (4), 85 (5) ($C_4H_5O_2^+$), 71 (7), 59 (12) ($C_3H_7O^+$), 43 (100) $C_2H_3O^+$)
1,2-*O*-Isopropylidene-[3-*C*,5-*O*,6-*O*-(methylmethylidyne)]-α-D-allofuranose (**11**)	244 (3) (M^+), 229 (8) ($M^+ - CH_3\cdot$), 187 (2), 186 (<1) ($M^+ - C_3H_6O$), 170 (1), 156 (<1) ($C_7H_8O_4$), 145 (1), 144 (<1) ($186 - C_2H_2O$), 127 (8), 126 (8) ($144 - H_2O$), 115 (4), 101 (1), 98 (38), 97 (16), 85 (21) ($C_4H_5O_2^+$), 73 (2), 71 (18), 61 (3), 60 (2), 59 (32) ($C_3H_7O^+$), 43 (100) (C_2H_3O)
Epimeric 3-*C*-(1^1-hydroxyethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranoses (**12a** and **12b**)	289 (11) ($M^+ - CH_3\cdot$), 275 (1), 271 (2) ($289 - H_2O$), 259 (2), 231 (6) ($289 - C_3H_6O$), 229 (3) ($289 - C_2H_4O_2$), 217 (2) ($275 - C_3H_6O$), 213 (2) ($231 - H_2O$), 203 (7) ($M^+ - C_5H_9O_2\cdot$), 201 (7) ($259 - C_3H_6O$), 189 (4), 187 (4), 185 (2), 171 (7), 169 (3), 157 (5), 153 (10), 144 (10), 131 (15), 127 (15), 115 (16), 113 (12), 101 (75) ($C_5H_9O_2^+$), 100 (23) ($C_4H_4O_3^+$), 99 (21), 97 (12), 85 (22) ($C_4H_5O_2^+$), 83 (13), 73 (14), 72 (20), 71 (40), 69 (14), 59 (76) ($C_3H_7O^+$), 57 (18), 55 (26), 43 (100) ($C_2H_3O^+$)
Epimeric 3,3^1-*O*-carbonyl-3-*C*-(1^1-hydroxyethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranoses (**13a** and **13b**)	315 (8) ($M^+ - CH_3\cdot$), 289 (<1), 287 (<1) ($315 - CO$), 285 (<1), 257 (2) ($315 - C_3H_6O$), 256 (4), 255 (1) ($315 - C_2H_4O_2$), 230 (1), 229 (1) ($330 - C_5H_9O_2\cdot$), 214 (1) ($315 - C_5H_9O_2\cdot$), 201 (3) ($229 - CO$), 197 (7) ($257 - C_2H_4O_2$), 185 (1), 171 (1), 153 (5), 140 (2), 131 (2), 125 (3), 111 (5), 101 (68) ($C_5H_9O_2^+$), 100 (4) ($C_4H_4O_3^+$), 85 (6) ($C_4H_5O_2^+$), 72 (26), 59 (20) ($C_3H_7O^+$), 55 (36), 43 (100) ($C_2H_3O^+$)

their melting points by 21.5°, but a mixed melting point showed a strong depression. Characteristic differences between **12a** and **12b** are evident in their X-ray powder diffraction patterns, and their n.m.r. and i.r. spectra. As expected, the mass spectra were indistinguishable. The minor, faster-migrating, higher-melting diol **12b** (m.p. 119–119.5°) gave an n.m.r. spectrum that was largely first-order and amenable to straightforward interpretation (see Table I), whereas the spectrum of the major, slower-migrating, lower-melting diol **12a** (m.p. 97.5–98°) was more complex because of extensive overlap of the signals for H-3^1,4,5, and 6. Both epimers showed two exchangeable protons and the expected spectral integrals. The stereochemical dispositions (*R* and *S*) at the new asymmetric center (C-3^1) generated in **12a** and **12b** remain to be determined.

Carbonylation of the diols **12a** and **12b** was effected with phosgene in pyridine, to give the corresponding, epimeric, cyclic carbonates **13a** and **13b** in high yield. These products contain the chain-branch functionality present in aldgarose. Both isomers were crystalline, gave acceptable elemental analyses, showed carbonyl absorption at ~5.5 μm typical of cyclic carbonates, and gave identical mass spectra. The epimers differed in m.p. by 52°, showed strong m.p. depression in admixture, and displayed characteristic differences in their X-ray powder diffraction patterns. Marked differences were also evident in the n.m.r. spectra; the spectrum of **13b** resembled that of the precursor **12b** in being largely first-order and amenable to straightforward assignment. In contrast, the spectrum of **13a** displayed overlapping resonances that were not readily assigned.

Interestingly, the specific rotations of **13a** and **13b** differed by only one degree. Furthermore, the o.r.d. spectra of the two products showed positive curves that, between 600 and 220 nm, were closely similar. As with the precursor diols, the stereochemistry at C-3[1] of **13a** and **13b** remains to be determined.

EXPERIMENTAL

General methods. — Evaporations were effected *in vacuo* at 40 ±5°. Melting points were determined with a Thomas–Hoover "Unimelt" apparatus and are uncorrected. G.l.c. was performed with a Beckman GC-5 dual-column instrument with flame-ionization detectors, and helium was used as the carrier gas. A column (3.18 mm × 1.83 m) of 3% SE-30 on Chromosorb P (80–100 mesh) was used, and the helium flow-rate was 65 ml.min^{-1}. The injector temperature was 210–220°; the column temperature is indicated in parentheses for each compound. Retention times (T_R) are given as adjusted values relative to the solvent peak ($T_R = 0$). T.l.c. was performed on 0.25-mm plates of Silica Gel G (Merck) activated at 110°, and 10% aqueous sulfuric acid was employed for detection. Column chromatography was conducted with silica gel No. 7734 (70–325 mesh) (E. Merck). Chromatographic solvents, unless otherwise indicated, were 1:1 ether–chloroform (*A*), or 1:2 ether–chloroform (*B*).

I.r. spectra were routinely recorded with a Perkin–Elmer Model 237 spectrophotometer; high-resolution i.r. spectra were recorded with a Perkin–Elmer Model 467 grating instrument. Optical rotations were determined with a Perkin–Elmer Model 141 polarimeter, with use of 1-dm tubes; optical rotatory dispersion measurements were made with a Jasco Model 5 instrument. N.m.r. spectra were recorded at 100 MHz with a Varian HA-100 or JEOL MH-100 instrument, with tetramethylsilane as the internal standard and the source of a lock signal. Chemical shifts are given on the τ scale, and the couplings recorded are first-order spacings. Mass spectra were measured with an AEI-MS-9 double-focusing, high-resolution, mass spectrometer, at an ionizing potential of 70 eV and an accelerating potential of 8 kV. A direct-insertion probe at 150–250° was employed. A Du Pont MS-21-490 instrument was employed for mass-spectrometric examination of g.l.c. peaks. Microanalyses were

performed by W. N. Rond. X-Ray powder diffraction data give interplanar spacings in Å for CuKα radiation (camera diameter = 114.59 mm). Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The three strongest lines are numbered (1 = strongest).

Solvents and reagents were of reagent grade. Tetrahydrofuran was distilled from lithium aluminum hydride, and pyridine was distilled from barium oxide; both were stored over Linde 4A molecular sieves prior to use.

*Preparation of 1,2:5,6-di-*O*-isopropylidene-α-*D*-ribo-hexofuranos-3-ulose* (**1**). — A solution of 10 g (36 mmoles) of 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose hydrate[15] (**1**) in 450 ml of toluene was boiled for 0.5 h under reflux, with azeotropic removal of water by distillation of ~50 ml of the solvent. The remaining solvent was evaporated off at 40°, to give the ketone (**1**) as a syrup. Drying for 8 h at 25°/5 torr gave pure **1**, showing negligible i.r. absorption in the O–H stretching region (2.88 μm) and a large peak at 5.73 μm (C=O stretch); it had $[\alpha]_D^{21}$ +101° (*c* 1, dry chloroform); lit.[31] $[\alpha]_D$ +107° (in chloroform). The product was found to be stable for ~3 months when stored over calcium sulfate in a vacuum desiccator, and was adequately pure for use as the starting material in the following step.

*3-*C*-Ethynyl-1,2:5,6-di-*O*-isopropylidene-α-*D*-allofuranose* (**2**). — Following an established procedure[4,11–13], ethylmagnesium bromide (50 mmoles) in dry tetrahydrofuran (prepared by diluting 18 ml of a 2.83M solution of the preformed reagent[32] in tetrahydrofuran to 120 ml) was added to a saturated solution of acetylene in tetrahydrofuran. Dry acetylene was bubbled through the solution for 45 min at ~25°, and then a solution of the ketone **1** (4.52 g, 17.5 mmoles) in tetrahydrofuran (20 ml) was added dropwise during 20 min, while a rapid flow of acetylene was passed through the continuously agitated solution, kept at ~25°. The resultant, cloudy mixture was stirred for 2 h (with continued passage of acetylene), and then cooled in an ice bath, and a saturated solution of ammonium chloride (~70 ml) was added slowly, with stirring, to decompose the Grignard complex. The mixture was washed with saturated, aqueous ammonium chloride (2 × 75 ml), and the aqueous phase was extracted with ether (2 × 25 ml). The extracts were combined, dried (magnesium sulfate), and evaporated to dryness, yielding **2** as a yellow solid. A solution of the product in ether (~15 ml) was passed through a short column (2 × 20 cm) of silica gel, and the column was eluted with ether (~200 ml)*. The eluate was evaporated, and the resulting solid was recrystallized from ether (7 ml per g of **2**), yielding 4.27 g (86%) of pure **2** in two crops; m.p. 106–107°, $[\alpha]_D^{21}$ +9.5° (*c* 1, chloroform); R_F 0.64 (solvent *A*); T_R 2.5 min (150°); λ_{max}^{KBr} 2.85 (OH), 3.08 (C≡C*H*), 3.34 (C*H*), 4.68 (C≡C), 7.25, 8.23, 9.75, 11.37, and 14.02 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 10.84 s, 7.30 s (3), 5.71 s (2), 5.37 w, 5.11 vw, 4.69 vs (1), 4.54 vw, 4.50 m, 3.94 m, 3.83 vw, 3.66 vw, 3.55 s, 3.48 w, and 3.32 w.

Anal. Calc. for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 59.44; H, 7.22.

*Alternatively, for preparations that were highly colored and contaminated with larger proportions of impurities (as shown by t.l.c.), column chromatography was effected on silica gel (~2 g of crude **12** per 100 g of silica gel) with 1:1 ether–chloroform as the eluant.

In one preparation, in which 9.5 g (33.5 mmoles) of **1** and ethylmagnesium bromide (105 mmoles) had been used, the acetylene flow was insufficient to maintain a saturated solution, and 2.34 g of an additional product, identified as 1,2-bis(1,2:5,6-di-*O*-isopropylidene-α-D-allofuranos-3-yl)acetylene (**3**) was isolated by column chromatography as described*; m.p. 163.5–164.5°, $[\alpha]_D^{21}$ −6.5° (*c* 2.3 chloroform); R_F 0.24 (solvent *A*); λ_{max}^{KBr} 2.91 (OH), 3.36 (C*H*), 7.26, 8.20, 9.33, and 11.42 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 13.80 m, 11.33 s, 9.50 m, 7.77 w, 6.52 s (3), 5.61 vs (1), 5.31 m, 5.05 m, 4.65 s (2), 4.43 m, 4.27 w, 4.14 w, 4.01 w, and 3.90 w.

Anal. Calc. for $C_{26}H_{38}O_{12}$: C, 57.56; H, 7.06. Found: C, 57.34; H, 7.09; Calc. for $C_{25}H_{35}O_{12}$ ($M^+ - 15$): *m/e* 527.2128; observed (high-resolution m.s.): *m/e* 527.2137.

Earlier fractions from the column gave the acetylene **2** (4.9 g); total conversion yield of **1** into (**2**+**3**), 60%.

3-C-Carboxy-1,2-O-isopropylidene-α-D-allofuranose-3^1*,5-lactone* (**5**). — A solution of 284 mg (1 mmole) of compound **2** in methanol (20 ml) was treated with an ozonized stream of oxygen (0.5 liter/min) for 30 min at 0°. The excess of ozone was now displaced by passing oxygen into the solution for 10 min, and then the solvent was evaporated off. The syrupy product was treated with *p*-toluenesulfonic acid (~5 mg) in boiling, 4:1 benzene–ethanol (60 ml) under reflux during 48 h, with gradual removal of a total of 20 ml of distillate. Sodium carbonate (~50 mg) was added with stirring, the salts were removed by filtration, and the filtrate was evaporated, giving a solid that was applied to a column (0.7 × 20 cm) of silica gel. Elution with chloroform (125 ml), followed by ether (125 ml), gave 151 mg (61%) of chromatographically homogeneous **5**. An analytical sample was prepared by recrystallization from 1:1 ether–hexane; m.p. 143–144.5°, $[\alpha]_D^{21}$ +34° (*c* 1, chloroform); R_F 0.37 (solvent *A*); λ_{max}^{KBr} (high resolution) 2.92 (OH), 3.38 (C*H*), 3.68 (C=O), 7.29, 7.92, 8.36, 8.50, 9.21, 9.67, 11.45, 12.81, and 14.69 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 9.89 vs (1), 8.24 w, 6.51 s, 5.79 w, 5.38 s (2), 4.81 s (3), 5.60 vw, 4.06 w, 3.87 m, 3.71 m, 3.56 m, 3.35 m, 3.25 m, 3.13 w, 2.97 w, and 2.80 m.

Anal. Calc. for $C_{10}H_{14}O_7$: C, 48.78; H, 5.73. Found: C, 48.61; H, 5.64.

3,6-Di-O-acetyl-3-C-carboxy-1,2-O-isopropylidene-α-D-allofuranose-3^1*,5-lactone* (**7**). — To a solution of **5** (75 mg, 0.30 mmole) in pyridine (5 ml) was added acetic anhydride (1 ml), and the mixture was stirred overnight. Methanol (~2 ml) was added, stirring was continued for 2 h, and the solvent was evaporated off. Addition of toluene (3 × 5 ml) to, and evaporation from, the residue gave a crystalline solid that was recrystallized from hexane containing a little ether, to give 88 mg (89%) of pure **7**; m.p. 113–113.5°, $[\alpha]_D^{22}$ +6.2° and $[\alpha]_{365}^{22}$ −33.0° (*c* 1.7, chloroform); R_F 0.72 (solvent *A*); λ_{max}^{KBr} (high resolution) 3.34, 3.36, 3.40 (C*H*), 5.58, 5.73, 5.76 (C=O), 7.31, 7.95, 8.20, 8.50, 9.61, and 11.48 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 12.99 vw, 12.02 w, 10.10 w, 8.36 vs (1),

*See footnote p. 311.

6.69 m, 6.17 m, 6.03 m, 5.82 m, 5.33 s (2), 4.69 s (3), 4.40 s, 4.15 vw, 3.97 w, 3.72 w, and 3.69 w.

Anal. Calc. for $C_{14}H_{18}O_9$: C, 50.91; H, 5.49. Found: C, 50.79; H, 5.51.

1,2:5,6-Di-O-isopropylidene-3-C-vinyl-α-D-allofuranose (**4**). — *A. By addition of vinylmagnesium chloride to 1,2:5,6-di-O-isopropylidene-α-D-ribo-hexofuranos-3-ulose* (**1**). A solution of 3 g (11.7 mmoles) of the ketone **1** in tetrahydrofuran (~20 ml) was added dropwise during 5 min, with stirring, to a solution of vinylmagnesium chloride (38 mmoles) [prepared by diluting 13.5 ml of a 2.84M solution of the commercial reagent in tetrahydrofuran (Ventron Corp., Beverly, Mass., U. S. A.) to ~30 ml with tetrahydrofuran]. Stirring was continued (under a reflux condenser) for 3 h, the mixture was cooled to 0°, and the excess of the Grignard reagent was decomposed by addition of saturated, aqueous ammonium chloride (~30 ml). Isolation and processing as described for **2** gave the product (**4**) as a syrup that was purified by chromatography on a column (3 × 60 cm) of silica gel with 1:1 ether–chloroform as the eluant. The eluate was evaporated to give a syrup, homogeneous by t.l.c., which was crystallized from ether (~8 ml) by slowly adding an equal volume of petroleum ether (b.p. 30–60°) and cooling to −20°; yield 0.96 g (29%); m.p. 66.5–67.5°, $[\alpha]_D^{21}$ +27.6° (*c* 1, chloroform); R_F 0.71 (solvent *A*); T_R 2.6 min (150°); λ_{max}^{KBr} 2.88 (OH), 3.35 (=C*H*), 7.28, 8.22, 9.37, 9.92, 10.71, 11.40, and 11.73 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 7.77 vs (1), 5.33 vw, 5.08 s (2), 4.55 m, 4.34 m, 3.82 w, 3.61 m, and 3.48 w.

Anal. Calc. for $C_{14}H_{22}O_6$: C, 58.73; H, 7.74. Found: C, 58.57; H, 7.70.

B. By reduction of 3-C-ethynyl-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (**2**) *with lithium aluminum hydride.* A solution of **2** (200 mg, 0.70 mmole) in tetrahydrofuran was treated with lithium aluminum hydride (~50 mg), and the mixture was boiled for 8 h under reflux, cooled, and the excess of reductant decomposed by addition of a few drops of 1:1 water–methanol. The salts were filtered off, and washed with ether, and the filtrate and washings were combined and evaporated to dryness, yielding a partly solid mass. Crystallization as described in the foregoing section gave 160 mg (79%) of pure **4**, identical (by m.p., mixed m.p., and $[\alpha]_D$) with the product isolated in part A.

trans-*1,2-Bis(1,2:5,6-di-O-isopropylidene-α-D-allofuranos-3-yl)ethylene* (**8**). — A solution of **3** (200 mg, 0.37 mmole) in tetrahydrofuran (30 ml) was boiled with lithium aluminum hydride (~50 mg) for 5 h under reflux. Addition of a few drops of 1:1 water–methanol, followed by removal of the salts by filtration, drying of the filtrate (magnesium sulfate), evaporation of the solvent, and drying at 25°/5 torr, gave 191 mg (96%) of crystalline and chromatographically homogeneous **8**. An analytical sample was prepared by recrystallization from ether; m.p. 253–255°, $[\alpha]_D^{21}$ 0° and $[\alpha]_{365}$ −16.2° (*c* 1, chloroform); R_F 0.43 (solvent *A*); λ_{max}^{KBr} 2.86 (OH), 3.35 (=C*H*), 7.31, 8.20, 8.65, 9.36, 9.79, 9.98, and 11.70 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 14.13 m, 11.36 m, 9.16 s (3), 7.13 vw, 6.65 s (2), 5.90 vw, 5.58 vs (1), 5.16 w, 5.07 vw, and 4.80 m.

Anal. Calc. for $C_{26}H_{40}O_{12}$: C, 57.35; H, 7.35. Found: C, 57.15; H, 7.16.

3-C-(Hydroxymethyl)-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (**6**). — *A. By ozonolysis–reduction of 1,2:5,6-di-O-isopropylidene-3-C-vinyl-D-allofuranose* (**4**). A solution of compound **4** (413 mg, 1.44 mmoles) in dry methanol was treated with an ozonized stream of oxygen (0.5 liter/min) for 1 h at −78°, at which time the solution had turned deep blue. Oxygen was passed through the solution to displace the ozone, and 75 mg (an excess) of sodium borohydride was added portionwise at 0° with stirring. After 30 min, the base was carefully neutralized with acetic acid, and the solvent was evaporated. Methanol (3 × 5 ml) was added to and evaporated from the residue (to decompose the borate complex), and the product was partitioned between water and chloroform. The dried (magnesium sulfate) organic layer was evaporated to a thick oil that was applied to a column (0.7 × 20 cm) of silica gel, which was then eluted with solvent *A*. Unreacted starting-material (**4**, 166 mg) was collected in the early fractions, followed by 182 mg (84%, taking the recovered **4** into account) of analytically pure **6**; m.p.* 62–63°, $[\alpha]_D^{23}$ +19.8° (*c* 1.1, chloroform); R_F 0.24 (solvent *A*); λ_{max}^{KBr} 2.88 (OH), 3.32 (C*H*), 7.27, 7.91, 8.20, 8.58, 9.40, 9.89, 11.44, and 11.86 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 13.53 m, 9.06 s (2), 7.48 m, 6.86 vw, 5.78 w, and 5.08 vs (1).

Anal. Calc. for $C_{13}H_{22}O_7$: C, 53.78; H, 7.64. Found: C, 53.67; H, 7.56.

B. By ozonolysis–reduction of 1,2-bis(1,2:5,6-di-O-isopropylidene-α-D-allofuranosyl-3-yl)ethylene (**8**). Under the conditions described in experiment *A*, compound **8** was ozonized for 30 min, and the product reduced to give, directly, a crystalline product that was homogeneous and indistinguishable from **6** by t.l.c. Recrystallization was effected by dissolving the product in 5 ml of ether, adding hexane, and boiling until a slight turbidity was produced; cooling to −20° gave 72 mg (64%) of crystals of pure **6**, identical in all respects with the compound described under *A*.

3,3¹-O-Carbonyl-3-C-(hydroxymethyl)-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (**9**). — To a solution of compound **6** (60 mg, 0.21 mmole) in pyridine (3 ml), cooled in an ice bath to 0°, was added a 12% solution of phosgene in benzene (0.60 ml). The mixture was stirred for 30 min, poured into ice–water (30 ml), and extracted with chloroform (3 × 5 ml). The extracts were combined, and evaporated, and toluene (3 × 5 ml) was added to and evaporated from the residue, to give 62 mg of a white solid. Crystallization from 1:1 ether–hexane gave 48 mg (73%) of analytically pure **9** as long needles; m.p. 116–116.5°, $[\alpha]_D^{22}$ +40.2° (*c* 2, chloroform); R_F 0.57 (solvent *A*); λ_{max}^{KBr} 3.40 (CH), 5.42, 5.50 (>C=O), 6.31, 7.24, 8.19, 9.02, 9.21, 9.80, 11.51, and 13.04 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 12.40 vs (1), 10.87 vw, 9.55 vw, 8.17 m, 7.20 w, 6.37 s (2), 5.82 m, 5.19 w, 4.73 s (3), 4.50 s, 4.19 m, 3.98 m, 3.77 m, and 3.47 w.

Note added in proof December 15th, 1973.* Compound **6 has been obtained by an independent route (A. J. Brink and A. Jordaan, *Carbohyd. Res.*, in press; A. Jordaan, personal communication) as a higher-melting dimorph, m.p. 74°. The present product, m.p. 62–63°, isolated as crystalline flakes, when recrystallized from hexane in the presence of a nucleus of Dr. Jordaan's product, was obtained as needles having m.p. 73.5–74.5°. The two samples gave identical mass-spectra.

Anal. Calc. for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 52.80; H, 6.55.

Oxymercurative hydration of 3-C-ethynyl-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (**2**). — To a solution of **2** (3.8 g, 13.4 mmoles) in ethyl acetate (380 ml) was added mercury(II) acetate (7.6 g, 23.8 mmoles). The resulting solution was stirred for 14 days at ~25°; t.l.c. (solvent *A*) then showed a single, non-migrating zone, with complete disappearance of starting material **2** (R_F 0.64). The product, apparently a mercury complex, was decomposed by passage of hydrogen sulfide for 5 min. After being kept for 30 min, the mixture was filtered through a Celite pad, and the filtrate was evaporated to dryness. The resulting syrup was applied to a column (2.5 × 50 cm) of silica gel and eluted with solvent *A* to give, after a void volume of 150 ml, three major components that were collected in 10-ml fractions. Fractions 18–23 gave 1.77 g (38%) of *3-C-acetyl-3-O-acetyl-1,2:5,6-di-O-isopropylidene-α-D-allofuranose* (**10**) as a viscous, non-distillable syrup, $[\alpha]_D^{21}$ +75.3° (*c* 1, chloroform); R_F 0.72 (solvent *B*); T_R 4.0 min (150°); λ_{max}^{neat} 3.33 (C*H*), 5.71, 5.82 (C=O), 7.30, 8.08, 9.33, 9.82, 11.45, and 11.88 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II.

Anal. Calc. for $C_{16}H_{24}O_8$: C, 55.81; H, 7.02. Found: C, 55.72; H, 6.99.

Fractions 24–27 gave 0.54 g (14%) of **2**, identical with authentic starting-material by m.p., i.r. spectroscopy, and mass spectrometry. Fractions 28–34 gave 1.27 g (39%) of *1,2-O-isopropylidene-[3-C,5-O,6-O-(methylmethylidyne)]-α-D-allofuranose* (**11**); m.p. 156–157°, $[\alpha]_D^{21}$ −34.4° (*c* 0.9, chloroform); R_F 0.44 (solvent *A*); T_R 1.9 min (150°); λ_{max}^{KBr} 2.88 (OH), 3.33, 3.35 (C*H*), 7.28, 8.06, 8.61, 9.10, 9.90, 10.68, 11.62, 12.00, and 14.28 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 10.13 m, 7.03 s (2), 5.67 w, 5.39 vw, 5.11 m, 4.89 vs (1), 4.70 vw, 4.49 s (3), 4.42 vw, 3.91 vw, 3.68 vw, 3.56 w, and 3.09 w.

Anal. Calc. for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 54.08; H, 6.34. Calc. for $C_{11}H_{16}O_6$: *m/e* 244.0947. Found (high resolution m.s.): *m/e* 244.0949.

The net-conversion yield (from **2**) into **10** plus **11** (taking into account recovered **2**) was 91%.

Attempted oxymercuration of 1,2:5,6-di-O-isopropylidene-3-C-vinyl-α-D-allofuranose (**4**). — Following the general procedure of Brown and Geoghegan[30], a solution of **4** (286 mg, 1 mmole) and mercury(II) acetate (319 mg, 1 mmole) in 1:2 tetrahydrofuran–water (15 ml) was stirred for 2 days at ~25°. The initial yellow color of the suspension did not change, indicating[30] incomplete reaction. The solution was boiled for 1 h under reflux, cooled, treated with 3M aqueous sodium hydroxide (1 ml) and 5M aqueous sodium borohydride (1 ml), saturated with sodium chloride, and the organic layer separated. The aqueous layer was extracted with ether (20 ml), and the extracts were combined, dried (magnesium sulfate), and evaporated, to give starting-material **4** (260 mg, 91%) identified by t.l.c. and by i.r. spectrum.

Various modifications of the foregoing process (for example, the use of more-concentrated solutions of reactants, or variation of the reaction time and temperature) failed to effect conversion of **4** into **12a** and **12b**.

Conversion of 3-C-acetyl-3-O-acetyl-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (**10**) *into 1,2-O-isopropylidene-[3-C,5-O,6-O-(methylmethylidyne)]-α-D-allofuranose* (**11**)

— *A. Saponification of* **10**. A sample (40 mg) of compound **10**, shown by both t.l.c. and g.l.c. to be free from **11**, was heated for 1 h under reflux with a 0.1M solution of sodium methoxide in methanol. Acetic acid was added to neutrality (pH ~6.5), and the solvent was evaporated off. T.l.c. analysis (solvent *A*) revealed a single, new zone (R_F 0.83) that migrated somewhat more slowly than **10** (R_F 0.90). G.l.c.–mass spectrometric analysis of the same mixture indicated a single component (T_R 3.6 min (150°)] that was eluted faster than compound **10** (T_R 4.0 min) and that, from its mass spectrum, appeared to be 3-*O*-deacetylated **10**; its mass spectrum showed a highest-mass peak at *m/e* 287 (16%, $M^+ - CH_3\cdot$, $C_{13}H_{19}O_7^+$) and a base peak at *m/e* 101 (100%, $C_5H_9O_2$), together with intermediate fragments [*m/e* 259 (8%), 229 (16), 201 (19), 172 (24), 143 (14), 131 (30), 129 (41), 111 (55), 85 (30), 71 (47), and 59 (75)] that could reasonably be assigned to fragmentations of the product derived by 3-*O*-deacetylation of **10**.

When the reaction was conducted at ~25°, saponification of **10** was not detected (by t.l.c.) after a reaction time of ~8 h, and the heating procedure described was needed in order to cause the conversion of **10** into the saponified product.

B. 5,6-Deacetonation of the saponification product of **10**, *and its conversion into* **11**. The crude, *O*-deacetylated **10** (~25 mg) was treated with 80% acetic acid (3 ml) for 12 h at 55 ±5°. T.l.c. analysis (solvent *A*) of the product obtained on evaporation of the solution showed a new product, R_F 0.16 (presumably, 5,6-deacetonated, 3-*O*-deacetylated **10**), but little of the anticipated, cyclized product **11** (R_F 0.44). A solution of the residue in abs. ethanol (5 ml) was boiled under reflux for 12 h, with the periodic removal of a few drops of ethanol–water azeotrope. Analysis of the product by t.l.c. and g.l.c. indicated formation of a substantial proportion (~35%) of the acetal **11**; R_F 0.44 (t.l.c.), T_R 1.9 min (150°), together with the component having R_F 0.16 (t.l.c.). G.l.c.–mass-spectrometric analysis of the mixture revealed a component [T_R 1.9 min (150°)] whose mass spectrum displayed the following peaks: *m/e* 244 (2%), 199 (6), 187 (2), 170 (1), 156 (1), 145 (1), 127 (11), 126 (11), 115 (4), 109 (7), 101 (2), 98 (43), 97 (21), 85 (20), 73 (2), 71 (2), 59 (34), and 43 (100). This fragmentation pattern is essentially that recorded for **11** (see Table II), and is identical in all respects to the spectrum obtained for authentic **11** when the pure compound was processed similarly.

The foregoing experiment was performed twice, and concordant results were obtained.

Epimeric 3-C-(1¹-hydroxyethyl)-1,2:5,6-di-O-isopropylidene-α-D-allofuranoses (**12a** *and* **12b**). — A solution of compound **10** (1.78 g, 5.18 mmoles) in tetrahydrofuran was boiled under reflux with lithium aluminum hydride for 36 h, with addition of a further portion of reductant (50 mg) after 24 h. The solution was cooled, the excess of reductant was decomposed by the addition of a few drops of saturated, aqueous ammonium chloride, the salts were filtered off and washed with hot chloroform (5 × 20 ml), and the organic extracts were combined and evaporated, to give 1.45 g (~92%) of recovered product, shown by t.l.c. to contain two slower-moving components, together with ~5% of material migrating like **10**. Chromatography on a column (3 × 60 cm) of silica gel with solvent *B* gave 250 mg of the pure, faster-moving

diol (**12b**) (R_F 0.45) and 450 mg of its pure, slower-migrating isomer (**12a**) (R_F 0.32), together with 678 mg of a mixture of **12a** and **12b**; total yield of **12b**, ~30%, and of **12a**, ~50%. Analytical samples of each were prepared by dissolution of a portion (100 mg) in ether (8 ml), with slow addition of hexane, and boiling to incipient turbidity. Cooling, initially at room temperature, and finally at 5°, gave, for **12b**, sharp needles, m.p. 119–119.5°, $[\alpha]_D^{25.4}$ +26.8° (*c* 1.7, chloroform); λ_{max}^{KBr} 2.81 (O*H*), 3.33 (C*H*), 7.28, 7.88, 8.26, 8.57, 8.88, 9.24, 9.62, 9.90, 11.39, and 11.72 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 10.51 vs (1), 7.54 m, 6.20 s (2), 5.60 m, 5.32 m, 4.94 vw, 4.53 s (3), 4.13 w, 3.93 vw, 3.74 w, 3.58 vw, 3.38 vw, and 3.27 m.

Anal. Calc. for $C_{14}H_{24}O_7$: C, 55.25; H, 7.95. Found: C, 55.38; H, 7.98.

Recrystallization of **12a** gave the product as a fluffy deposit of fine needles, m.p. 97.5–98°, $[\alpha]_D^{25.4}$ +14.3° (*c* 1.1, chloroform); λ_{max}^{KBr} 2.88 (O*H*), 3.33 (C*H*), 7.36, 8.00, 8.32, 8.67, 9.40, 9.91, 11.44, and 11.69 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 14.19 w, 9.96 vs (1), 8.03 m, 7.20 s (2), 5.96 w, 5.88 w, 5.40 w, 5.03 s (3), 4.76 vw, 4.59 m, 4.29 vw, 4.27 m, 4.06 vw, 3.72 vw, and 3.60 m.

Anal. Calc. for $C_{14}H_{24}O_7$: C, 55.25; H, 7.95. Found: C, 55.32; H, 7.86.

A mixture of **12a** and **12b** melted at 87–90°.

A small-scale reduction of **10** (~10 mg) with sodium bis(2-methoxyethoxy)-aluminum hydride ("Vitride", Eastman Chemicals) (0.25 ml) in refluxing tetrahydrofuran (5 ml) was processed as in the foregoing experiment, and the product analyzed by g.l.c.–mass spectrometry; this revealed that the major product (~3 parts) was the product of ester cleavage, namely, 3-*C*-acetyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose [T_R 4.6 min (150°)]; *m/e* 287 (6%) ($M^+ - \cdot CH_3$), 259 (2) ($M^+ - -C_2H_3O$), 229 (3), 201 (3), 172 (8), 143 (3), 131 (12), 129 (13), 111 (14), 101 (45), 85 (9), 71 (21), 59 (37), and 43 (100). The minor product (~1 part) was a mixture of the diols **12a** and **12b** [T_R 7.3 min (150°)] as indicated by the mass spectrum.

Similarly, compound **10** (10.0 mg) was treated with sodium borohydride (5 mg) in ethanol (5 ml) at 25°. Analysis by g.l.c.–mass spectrometry then showed only a small proportion (~15%) of the expected reduction product, 3-*O*-acetyl-3-*C*-(1[1]-hydroxyethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose [T_R 6.1 min (150°)] as indicated by its mass spectrum; *m/e* 331 (3%) ($M^+ - \cdot CH_3$), 315 (6), 271 (1), 257 (4), 245 (1), 229 (5), 227 (5), 171 (23), 143 (10), 101 (44), 85 (10), 59 (30), and 43 (100).

The remaining products were the diols **12a** plus **12b** (~10%) [T_R 7.3 min (150°)], together with a large proportion (~75%) of unreacted starting-material **10** [T_R 4.0 min (150°)], as indicated by their retention times and mass spectra.

Epimeric 3,1[1]-O-carbonyl-3-C-(1[1]-hydroxyethyl)-1,2:5,6-di-O-isopropylidene-α-D-allofuranoses (**13a** *and* **13b**). — Under anhydrous conditions, a 12.5% solution of phosgene in benzene (2.2 ml) was added to a solution of **12a** (218 mg, 0.72 mmole) in pyridine (10 ml) cooled to 0°. Stirring was continued for 0.5 h at room temperature, and then the mixture was poured into ice–water, with stirring. The mixture was

extracted with chloroform (3 × 10 ml), and the extracts were combined, dried (magnesium sulfate), evaporated, and toluene (3 × 10 ml) added to and distilled from the residue. Trituration with ether gave a mass of white needles; these were recrystallized from 1:1 ether–petroleum ether (b.p. 30–60°) to give 189 mg (80%) of analytically pure **13a**; m.p. 153–154°, $[\alpha]_D^{25.4}$ +26.4°; $[\alpha]_{500}$ +30.3°, $[\alpha]_{400}$ +69.7°, $[\alpha]_{300}$ +178°, and $[\alpha]_{250}$ +349° (*c* 1.8, chloroform); R_F 0.52 (solvent *B*); λ_{max}^{KBr} 3.55 (C*H*), 5.54 (C=O), 7.27, 7.44, 7.90, 8.24, 8.74, 9.41, 9.99, 11.52, 11.82, and 13.08 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 9.02 m, 8.41 m, 7.59 m, 6.80 vs (1), 6.26 m, 5.63 vw, 5.27 s (2), 4.84 w, 4.62 s (3), 4.44 vw, 4.18 m, 3.94 m, 3.76 w, 3.52 w, and 3.36 w.

Anal. Calc. for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.22; H, 6.58.

Carbonation of **12b** (230 mg, 0.76 mmole), as already described for **12a**, was effected by using a 12.5% solution of phosgene in benzene (2.3 ml). Recrystallization of the product gave 207 mg (83%) of pure **13b**; m.p. 205–205.5°, $[\alpha]_D^{25.4}$ +25.4°; $[\alpha]_{500}$ +40.6°, $[\alpha]_{400}$ +118°, $[\alpha]_{300}$ +304°, and $[\alpha]_{250}$ +473° (*c* 1.3, chloroform); R_F 0.46 (solvent *A*); λ_{max}^{KBr} 3.34 (C*H*), 5.52 (C=O), 7.25, 7.92, 8.22, 8.68, 9.30, 9.90, 11.52, 11.83, 12.94, and 13.30 μm; for n.m.r. data, see Table I; for mass-spectral data, see Table II; X-ray powder diffraction data: 8.64 s (3), 7.16 m, 6.46 vs (1), 5.39 m, 5.11 w, 4.84 s (2), 4.34 m, 4.15 vw, 3.99 w, 3.82 w, 3.61 m, and 3.48 w.

Anal. Calc. for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.45; H, 6.70.

A mixture of **12a** and **13b** melted at 125–128°.

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