Carbohydrate Research, 136 (1985) 37–52
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE ISOPROPYLIDENATION OF D-RIBOSE DIETHYL DITHIOACETAL AND RIBITOL. A NEW SYNTHESIS OF α- AND β-D-RIBOFURANOSYLETHYNE *via* 2,3:4,5-DI-*O*-ISOPROPYLIDENE-*aldehydo*-D-RIBOSE*

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(Received March 26th, 1984; accepted for publication, May 16th, 1984)

ABSTRACT

The reaction of D-ribose diethyl dithioacetal with acetone and sulphuric acid in the presence of anhydrous copper sulphate gives the 2,3:4,5-di-*O*-isopropylidene derivative **14** (40%) and the isomeric 2,5:3,4-di-*O*-isopropylidene acetal **17** (40%), contrary to the conclusions of some previous investigators. Earlier work on the structures of the mono-*O*-isopropylidene derivatives formed when copper sulphate alone is the catalyst has been confirmed and extended. The diacetonides **14** and **17** were converted into the *aldehydo*-D-ribose derivatives **11** and **30**, respectively, and thence into the di-*O*-isopropylideneribitol derivatives **24** and **25**. When ribitol was treated with acetone and sulphuric acid, 1,2:4,5-di-*O*-isopropylideneribitol (66%) was the major product, together with DL-**24** (22%) and DL-**25** (11%). The *aldehydo*-D-ribose **11** reacted with ethynylmagnesium bromide in tetrahydrofuran to give the D-*altro* and D-*allo* alcohols **39** and **40** in the ratio 2:1. Toluene-*p*-sulphonylation of the mixture of **39** and **40**, followed by solvolysis in buffered, boiling aqueous ethanol, afforded the 2,3-*O*-isopropylidene-D-ribofuranosylethynes **45** and **46** with loss of the terminal *O*-isopropylidene group. ^{13}C-N.m.r. spectroscopy was used extensively to determine the ring sizes of the isopropylidene derivatives.

INTRODUCTION

In earlier papers in this series[1], we have developed general syntheses of *C*-nucleoside antibiotics[2–5] using 2,3,5-tri-*O*-benzyl-D-ribofuranose (**1**) as starting material. The reaction of **1** with ethynylmagnesium bromide affords a mixture of epimeric diols **2** which can be cyclised using toluene-*p*-sulphonyl chloride in pyridine to give a mixture of tri-*O*-benzyl-β- and -α-D-ribofuranosylethyne[6]. Using this and other Grignard reagents, the acetylenic intermediates **3–6** have become

*C-Nucleoside Studies, Part 16. For Part 15, see ref. 1.
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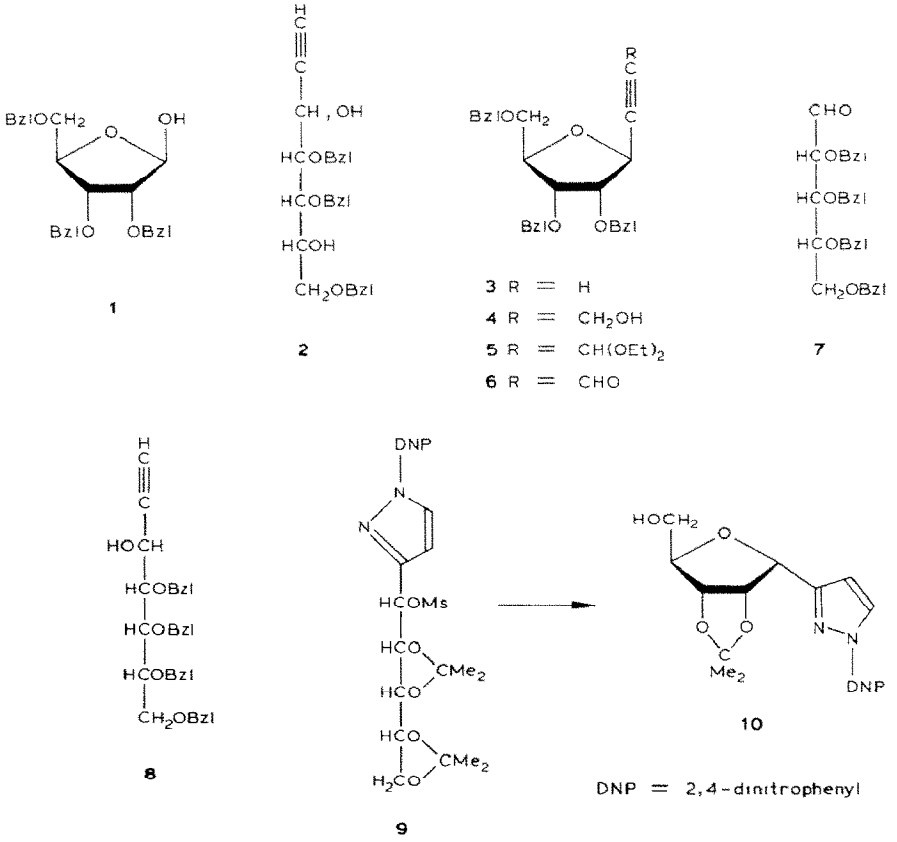
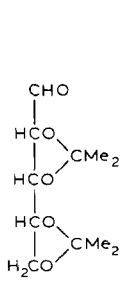
0008-6215/85/$ 03.30

available[6–8]. The formation of furanoid derivatives of D-*ribo* configuration depends critically on the regioselective toluene-*p*-sulphonylation of O-3 in such diols as **2**. As an alternative, we recently studied[9] the reaction of 2,3,4,5-tetra-*O*-benzyl-*aldehyde*-D-ribose (**7**) with ethynylmagnesium bromide. Cyclisation of the resulting D-*altro* alcohol **8** gave[9] the β-anomer **3**, with loss of the 6-*O*-benzyl group *via* benzyloxy participation[10]. By this means, the problem of regioselective toluene-*p*-sulphonylation was avoided, but unfortunately the initial Grignard reaction was non-stereoselective, affording equal amounts of **8** and its D-*allo* epimer; the latter formed the α-D-ribofuranosyl derivative, of less value as a *C*-nucleoside precursor, on ring closure.



Related work[11] showed that the di-*O*-isopropylidene derivative **9** underwent ring closure, with simultaneous loss of the terminal isopropylidene group, to give the α-D-ribofuranosyl derivative (**10**). We therefore wished to study the reaction of 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-ribose (**11**) with ethynylmagnesium bromide followed by cyclisation. We have shown[12] that 2,3-*O*-isopropylidene-D-ribose (**12**) reacts with ethynylmagnesium bromide to give the *allo*-triol (**13**) almost exclusively. Ogura and his co-workers[13] have described the reaction of **11** with



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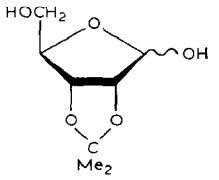

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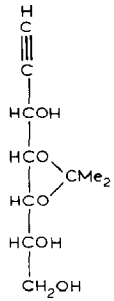

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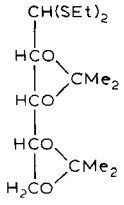

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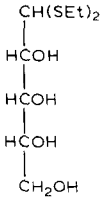

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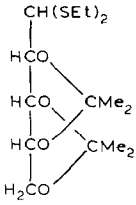

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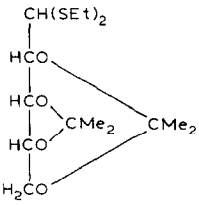


17

ethynylmagnesium bromide but, as will be shown below, there is some doubt as to the structure of their starting material.

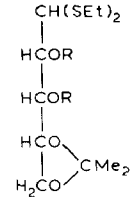
The most obvious source of the aldehyde **11** was 2,3:4,5-di-*O*-isopropylidene-D-ribose diethyl dithioacetal (**14**). The isopropylidenation of D-ribose diethyl dithioacetal[14,15] (**15**) has been described several times[13,16–18]. In 1963, Foster and his colleagues[16] reported that isopropylidenation of **15** under acidic conditions gave a diacetal whose precise structure was not established and was designated simply as a 2,3,4,5-di-*O*-isopropylidene compound. Later workers[13,17–19] and some reviewers[20] have apparently believed that the structure of the diacetal was fully established[16] as the 2,3:4,5-diacetal **14**. More-detailed work[21,22] by Foster's group, directed mainly towards the di-*O*-isopropylidene derivatives of ribitol, indicated that the diacetal had the 2,4:3,5 structure **16**. Apart from the review by Clode[23], these later papers appear to have been ignored by subsequent workers, but van Es and his co-workers[18] independently ascribed structure **16** to one product of isopropylidenation of **15**.

We have therefore reinvestigated the isopropylidenation of **15** under several conditions and established the structures of the products; in parallel, the behaviour of ribitol has been examined[24]. A study of the reaction of ethynylmagnesium bromide with **11**, our original objective, was then pursued.

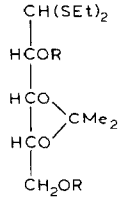
RESULTS AND DISCUSSION

In our hands, isopropylidenation of **15** with acetone, using a mixture of sulphuric acid and anhydrous cupric sulphate as catalyst[16], gave a product which could be resolved into two major components in t.l.c. Chromatography on silica gel gave, first, the 2,3:4,5-diacetal **14** (40%), $[\alpha]_D$ −94° (chloroform), whose structure was elucidated using ^{13}C-n.m.r. spectroscopy[24,25]. Signals for the quaternary acetal carbon atoms appeared at δ 109.5 and 108.9, characteristic of *O*-isopropylidene groups containing a 5-membered ring. The $[\alpha]_D$ value differed from that [−4° (chloroform)] ascribed to **14** by van Es[18]. Further elution gave the 2,5:3,4-diacetal **17** (40%), $[\alpha]_D$ −21.5° (chloroform), whose structure was also determined by ^{13}C-n.m.r. spectroscopy. Signals for the quaternary acetal carbon atoms appeared at δ 108.1 and 101.6, shifts typical[26] of 5- and 7-membered rings, respectively. We were unable to detect any of the 2,4:3,5-diacetal **16**, whose ^{13}C-n.m.r. spectrum would have been easily recognised[26]. The $[\alpha]_D$ value [−60° (chloroform)] reported by van Es and co-workers[18] for **16** is quite different from that of **17**. It is interesting to note that the $[\alpha]_D$ value (−53°) reported by Foster and co-workers[16] for their diacetonide is close to the figure (−57.5°) to be expected from a 1:1 mixture of **14** and **17**.

Both van Es[18] and Jones[17] and their collaborators used anhydrous cupric sulphate as the sole catalyst. In order to resolve the discrepancies with the work of van Es, we decided to follow these conditions; it is known[23] that such reactions are more under kinetic control. The reaction mixture appeared to reach a steady state (t.l.c.) after 16 h and was not significantly changed up to 36 h. The major products were two monoacetals; a third monoacetal and two diacetals, with chromatographic mobilities identical to those of **14** and **17**, were minor products. After chromatography, the diacetal fraction (3%) was shown by ^{13}C-n.m.r. spectroscopy to be a 1:1 mixture of **14** and **17**; no signals attributable to the 2,4:3,5-isomer **16** were detected. Jones and co-workers[17] reported small proportions of two diacetonides in their reaction mixture. The major monoacetal product was the 4,5-*O*-isopropylidene derivative **18** (33%) which had been isolated and characterised[17]. Its structure was confirmed by ^{13}C- and ^{1}H-n.m.r. data. The signal due to the quaternary acetal carbon atom appeared at δ 109.4, typical of a 5-membered cyclic acetal[26]. The ^{1}H-n.m.r. spectrum of the derived diacetate **19** contained two low-field signals, each a doublet of doublets, at δ 5.36 and 5.66, due to H-3 and H-2, respectively. Further elution gave a second monoacetal, the 3,4-*O*-isopropylidene compound **20** (1%), whose ^{13}C-n.m.r. spectrum showed a signal at δ 108.4 due to a five-membered acetal ring. The ^{1}H-n.m.r. spectrum of the diacetate **21** showed a low-field triplet, assignable to H-2. Finally, further elution gave the 2,4-acetal **22** (26%), previously isolated by Jones and co-workers[17]. The presence of a 6-membered acetal ring was clearly shown by ^{13}C-n.m.r. spectroscopy [signals at δ 19.3 (axial Me), 29.0 (equatorial Me), and 99.1 (quaternary C)][26]. The diacetate **23** exists in the chair conformation **23C**; its ^{1}H-n.m.r. spectrum contains only one low-field signal, a triplet at δ



18 R = H
19 R = Ac



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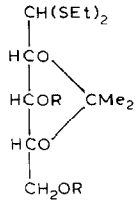
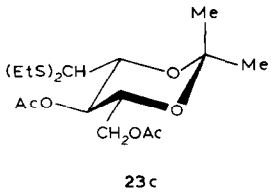
21 R = Ac



22 R = H
23 R = Ac

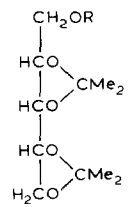


23c

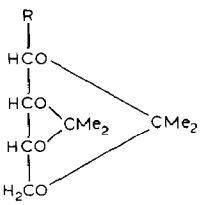
5.18 for H-3 ($J_{2,3} = J_{3,4} = 9.5$ Hz), indicating that H-2, H-3, and H-4 are all axial.

These results agree very closely with those of Szarek *et al.*[17], but we have been unable to confirm the properties of the di-*O*-isopropylidene compounds described by van Es and co-workers[18]. It was of interest to examine the reaction of **15** with 2,2-dimethoxypropane under conditions of kinetic control. The major product was the 2,3:4,5-diacetal **14** (65%) and the minor product the 2,5:3,4-diacetal **17** (30%). Again, there was no evidence for the presence of the 2,4:3,5-diacetal **16**.

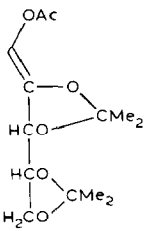
These structural revisions clearly had consequences for the structures of the products of reaction of ribitol with acetone[16,21,22]. The diethyl dithioacetals **14** and **17** were therefore converted into the corresponding ribitol derivatives **24** and **25** to be used as reference compounds. Demercaptalation of **14** in aqueous acetone in the presence of mercuric chloride and mercuric oxide gave the aldehydo sugar **11** (70%), $[\alpha]_D$ −17° (chloroform), whose structure was shown by ^{1}H-n.m.r. spectroscopy; in particular, the aldehyde proton appeared as a doublet at δ 9.72. It is interesting to note that the only previous evidence convincingly in favour of the 2,3:4,5-diacetonide structure **11** was the reaction with acetic anhydride and sodium acetate to give the enol acetate **26**[19], which was also obtained from the known[27] 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose (**27**). More recently, **11** has been synthesised[28] from 2,3-*O*-isopropylidene-D-glyceraldehyde by stereoselective chain extension. Reduction of **11** with sodium borohydride gave the alcohol **24**[29] (61%), which was converted into the crystalline benzoate **28**, m.p. 82–83°, $[\alpha]_D$ −33.3° (chloroform), and toluene-*p*-sulphonate **29**.



24 R = H
28 R = Bz
29 R = Ts



25 R = CH_2OH
30 R = CHO
31 R = CH_2OBz



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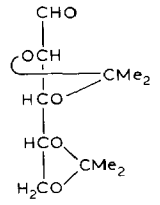

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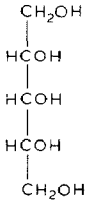
Demercaptalation of **17** gave the aldehydo sugar **30** (57%), $[\alpha]_D$ −54° (chloroform), which was reduced with sodium borohydride to give the crystalline alcohol **25**, m.p. 94–100°, $[\alpha]_D$ −84° (chloroform), whose benzoate **31**, $[\alpha]_D$ −70° (chloroform), did not crystallise. It is clear from these results that the crystalline *O*-benzoyl-di-*O*-isopropylideneribitol, m.p. 79–80°, $[\alpha]_D$ −32°, derived by Foster and co-workers[16] from their di-*O*-isopropylidene-D-ribose diethyl dithioacetal was **28**, *i.e.*, the 2,3:4,5 isomer*.

The reaction of ribitol (**32**) with acetone in the presence of concentrated sulphuric acid was then studied. Chromatography on silica gel resolved the product into two fractions, A and B. The ^{1}H-n.m.r. spectrum of fraction A in dimethyl sulphoxide-d_6 indicated that it was a mixture of two alcohols, one primary and one secondary, since there were two signals for exchangeable protons, one a triplet at δ 4.50 and the other a doublet at δ 5.15. When fraction A was treated with benzoyl chloride (0.5 mol. equiv.) in pyridine, it yielded a crystalline benzoate, m.p. 71°, in 21% yield; it was easily separated from unreacted secondary alcohol by chromatography on silica gel. Its ^{1}H- and ^{13}C-n.m.r. spectra were identical with those of **28**, proving it to be DL-**28**, corresponding to the primary benzoate, m.p. 73–74°, isolated by Foster and co-workers[16] from a related procedure. The recovered, unreacted secondary alcohol was shown to be **33**[21,22] by treatment with excess of benzoyl chloride in pyridine The resulting crystalline monobenzoate, m.p. 69–71°, was studied by n.m.r. spectroscopy. The simplicity of the ^{1}H- and ^{13}C-n.m.r. spectra established the symmetrical structure **34**; the ^{13}C-n.m.r. spectrum, in particular, contained signals corresponding to two equivalent dioxolane rings. This benzoate, m.p. 69–71°, was previously isolated from the products of isopropylidenation of ribitol and its structure fully determined[21,22].



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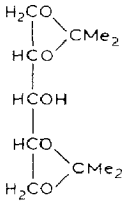
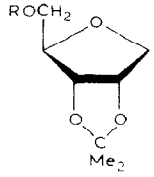


33 R = H
34 R = Bz

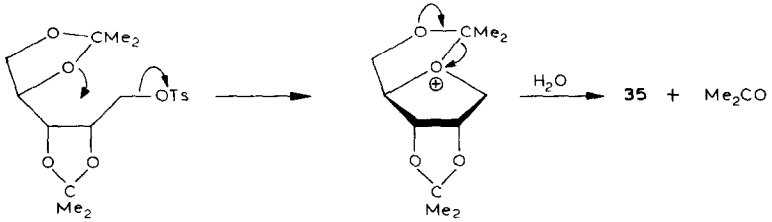


35 R = H
36 R = Ts

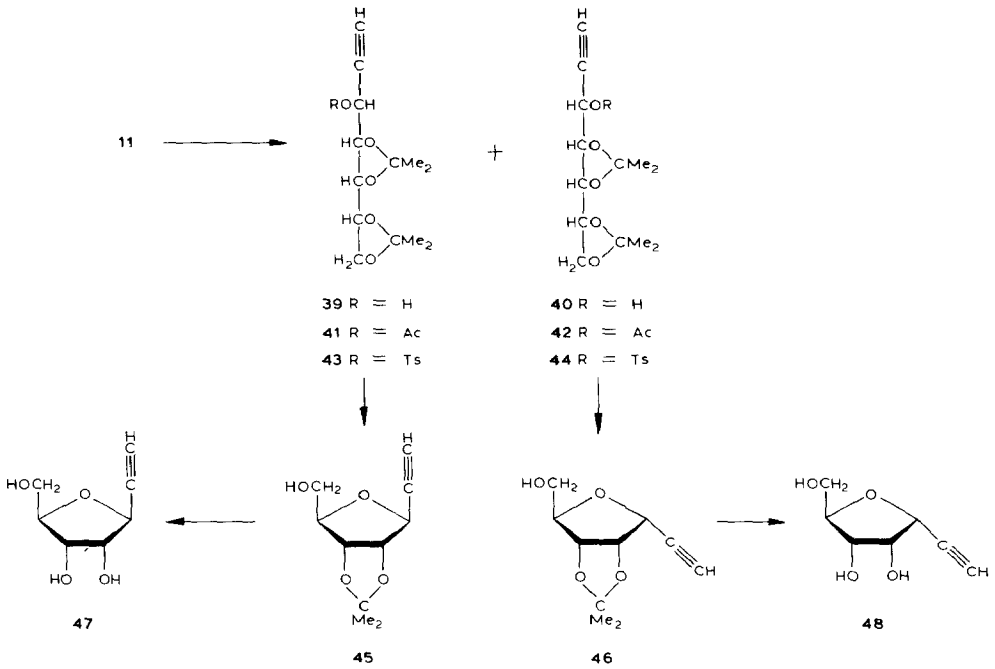
Fraction B (11%) was a single compound which crystallised on standing, and had m.p. 105–107°. Its ^{1}H- and ^{13}C-n.m.r. spectra and chromatographic properties were identical to those of the primary alcohol **25**, proving it to be DL-**25**. This isomer had not been detected by the earlier workers. The relative amounts of DL-**24**, **33**, and DL-**25** were ~2:6:1.

*To avoid confusion, derivatives of ribitol are regarded as being derived from ribose, without change of numbering of the carbon atoms. Thus, **24** is named 2,3:4,5-di-*O*-isopropylidene-D-ribitol and not 1,2:3,4-di-*O*-isopropylidene-L-ribitol

We next studied the behaviour of the toluene-*p*-sulphonate **29** as a model for cyclisation to give D-ribofuranosyl derivatives. As expected[9,11], it was unstable at room temperature. When treated with sodium benzoate in boiling *N,N*-dimethylformamide, the benzoate **28** was isolated (57%) together with 1,4-anhydro-2,3-*O*-isopropylidene-D-ribitol (**35**, 40%). The latter was converted into the crystalline toluene-*p*-sulphonate **36**, identified by comparison with DL-**36**, prepared from 1,4-anhydro-DL-ribitol[30]. Under solvolytic conditions (50% aqueous ethanol in the presence of calcium carbonate), **29** was converted into **35** as the only isolable product. The processes represented by **37** and **38** are presumably involved[9,11].



The reaction of the *aldehydo*-D-ribose **11** with ethynylmagnesium bromide in tetrahydrofuran was then examined. A mixture of *altro* and *allo* alcohols, **39** and **40**, was obtained, in 81% yield. The presence of two epimers was detected after the formation of **41** and **42** by acetylation of the crude product; the ^{1}H-n.m.r. spectrum



showed two signals for OAc groups, at δ 2.10 and 2.08 in the ratio 2:1. The mixture of alcohols, **39** and **40**, was treated with toluene-*p*-sulphonyl chloride in pyridine, yielding a mixture of sulphonates, **43** and **44**, in 70% yield. They could not be separated chromatographically and, as expected, were unstable at room temperature. The freshly prepared sulphonates were subjected to solvolysis by heating in aqueous ethanol in the presence of calcium carbonate. Chromatography of the products on silica gel yielded the β-D-ribofuranosylethyne **45** (60%) and the α isomer **46** (27%) as syrups having chromatographic and spectroscopic properties identical to those previously recorded[12,31]. Acid hydrolysis of **45** and of **46** gave β-D-ribofuranosylethyne (**47**) and the α isomer **48**, respectively.

The stereoselectivity of the reaction of **11** with ethynylmagnesium bromide, giving an *altro:allo* ratio of ~2:1, is in marked contrast to the behaviour[12] of the mono-*O*-isopropylidene compound **12** where the ratio is ~1:9. The Cram cyclic model (**49**→**50**)[6,32–34], which leads to the *threo* product preferentially, may be invoked for **11**, but it appears that, for **12**, a stronger binding, such as in **51**→**52**, is involved. It should be emphasised that these are complex systems because of the presence of several ether oxygens[35]. We have recently relied[36] on the strong stereoselectivity of the reaction of **12** with other Grignard reagents in a new synthesis of the antibiotic anisomycin.

Although the reaction of **11** with ethynylmagnesium bromide affords a route to β-D-ribofuranosylethyne, the preparation of **11** is somewhat tedious compared to that of **1**. Our earlier methods[6–8], leading to the *C*-nucleoside intermediates **3** and **5**, are therefore preferred.

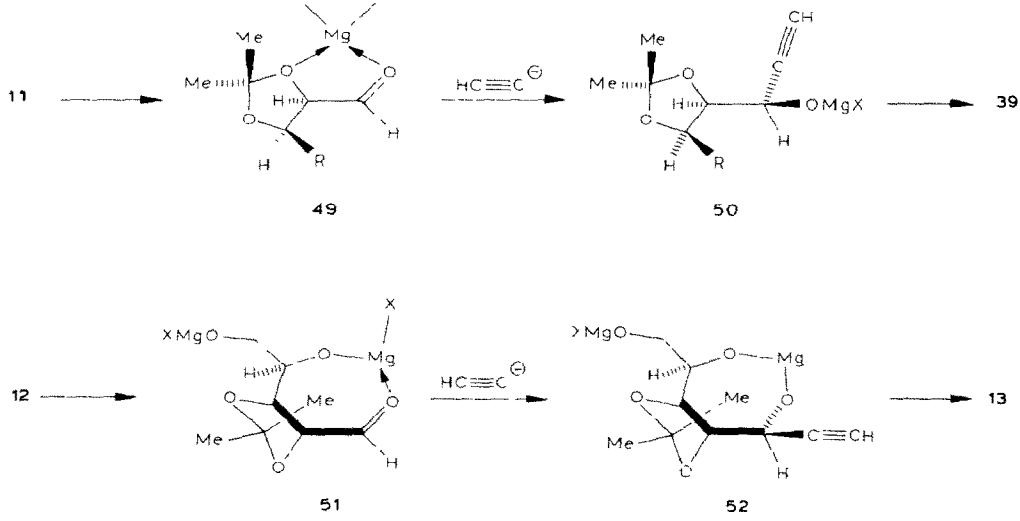


TABLE I

CHEMICAL SHIFTS[a] FOR ISOPROPYLIDENE ACETALS

Compound	*Acetal carbon*	*C=O*	*Aromatic carbons*	*Sugar carbons*	Me-*Ar*	Me*CO*	*SCH*$_2$Me	*SCH*$_2$*Me and* gem-*Me*$_2$	$\Delta\delta$ gem-*Me*$_2$
14	108.9[b]			50.2,68.1,73.0,			13.9	24.5(×2),25.0,25.3,	≤2.1[b]
	109.5[b]			78.9,81.3			14.2	26.4,26.6	
17	101.6[c]			52.3,58.0,73.2,			14.1	(23.5,28.2)[c]	4.7[c]
	108.1[b]			76.4(×2)			14.3	24.6,25.1(×2),25.6	≤1.0[b]
18	109.0[b]			54.5,65.2,71.2,			14.3	25.1(×2),25.5,	≤1.2[b]
				74.4,76.2			14.6	26.3	
19	109.4[b]	169.5		51.4,65.9,71.8,		20.5	14.0	24.2,24.7,25.2,	≤1.8[b]
		169.6		72.9,73.5		20.6	(×2)	26.0	
20	108.4[b]			54.4,60.6,71.4,			14.3	25.1,25.6,26.1,	≤2.7[b]
				76.6,77.2			14.5	27.8	
22	99.1[d]			52.5,63.0,65.7,			14.4	(19.3,29.0)[d]	9.7[d]
				73.0,77.5			(×2)	25.2,25.4	
23	99.2[d]	169.4		52.3,63.7,65.6,		20.7	14.2	(19.0,28.9)[d]	9.9[d]
		170.7		70.1,76.4		(×2)	14.4	25.2,25.4	
25	101.7[c]			63.4,70.2,75.3,				(23.7,28.2)[c]	4.5[c]
	108.5[b]			76.2,76.5				(25.0,25.7)[b]	0.7[b]
28	109.2[b]	166.2	128.2(×2),129.6(×2),	63.3,68.0,73.2,				25.2,25.3,26.7,	≤2.5[b]
	109.7[b]		130.1,132.8	75.4,77.9				27.7	
29	109.6[b]		128.0(×2),129.6(×2),	65.5,67.9,73.0,	21.5			24.9,25.9,26.7,	≤2.5[b]
	109.8[b]		133.1,144.6	74.3,77.4				27.4	
34	109.5[b]	165.6	128.3(×2),129.7(×3),	65.8(×2),73.1,				24.9(×2),26.2(×2)	1.3[b]
	(×2)		133.1	74.7(×2)					

[a]In chloroform-*d*; p.p.m. downfield from Me_4Si. [b]1,3-Dioxolane ring. [c]1,3-Dioxepane ring. [d]1,3-Dioxane ring.

EXPERIMENTAL

^{1}H-N.m.r. spectra were recorded at 100 MHz with a Jeol HA100, and at 220 MHz with a Varian HR220 spectrometer (at PCMU, Harwell). ^{13}C-N.m.r. spectra were recorded at 20 MHz with a Varian CFT-20 spectrometer (University of Edinburgh); the results are shown in Table I. T.l.c. was carried out on Kieselgel 60 HF 254 (Merck). Adsorption chromatography was carried out using silica gel (Merck, 70–230 mesh ASTM). Light petroleum refers to the fraction b.p. 60–80°. Specific rotations refer to room temperature (20–25°) and were measured with a Bendix-NPL 143D automatic polarimeter (path-length, 1 cm).

Isopropylidenation of D-*ribose diethyl dithioacetal*[16] (**15**). — A mixture of **15** (14 g), anhydrous copper sulphate (18.7 g), conc. sulphuric acid (3.3 mL), and acetone (515 mL) was stirred for 10 h at room temperature, neutralised with aqueous ammonia, filtered, and concentrated *in vacuo*. The residue was partitioned between chloroform and water, and the dried chloroform extracts were concentrated to yield a syrup (18 g) which was eluted from silica gel with light petroleum–ether (4.7:1) to give, first, the 2,3:4,5-diacetal **14** (7.35 g, 40%) as a syrup, $[\alpha]_D$ −94° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.20–1.64 (m, 18 H, 2 CMe_2 and 2 SCH_2Me), 2.74 (q, 4 H, 2 SCH_2Me), and 3.72–4.76 (m, 6 H).

Anal. Calc. for $C_{15}H_{28}O_4S_2$: C, 53.56; H, 8.39; S, 19.04. Found: C, 53.58; H, 8.29; S, 18.93.

Eluted second was the syrupy 2,5:3,4-diacetal **17** (7.35 g, 40%), $[\alpha]_D$ −21.5° (*c* 0.9, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.16–1.64 (m, 18 H, 2 CMe_2 and 2 SCH_2Me), 2.72 (q, 4 H, 2 SCH_2Me), and 3.92–4.48 (m, 6 H).

Anal. Found: C, 53.43; H, 8.40; S, 18.98.

Isopropylidenation of **15**. — *(a) Under conditions of kinetic control.* The thioacetal **15** (5 g) was stirred with 2,2-dimethoxypropane (50 mL) and acetone (100 mL) in the presence of toluene-*p*-sulphonic acid (1 g) for 10 min. The mixture was then neutralised (Na_2CO_3). Isolation using chloroform, followed by chromatography on silica gel and elution with light petroleum–ether (49:1), yielded the 2,3:4,5-diacetal **14** (4.3 g, 65%), followed by the 2,5:3,4-diacetal **17** (2 g, 30%). The compounds were identical (t.l.c., ^{1}H- and ^{13}C-n.m.r. spectra) to the samples described above.

(b) Employing anhydrous copper sulphate as catalyst. Compound **15** (2 g) in dry acetone (15 mL) was stirred in the presence of anhydrous copper sulphate (3 g) for 16 h. The solution was filtered and concentrated *in vacuo* to yield a syrup, which was eluted from silica gel with light petroleum–ether (9:1) to give a syrupy equimolar mixture (0.08 g, 3%) of the acetals **14** and **17**. ^{13}C-N.m.r. data ($CDCl_3$): δ 101.7, 108.2 109.0, and 109.6 (quaternary carbon atoms only).

Elution with light petroleum–ethyl acetate (4:1) then gave the 4,5-acetal **18** (0.75 g, 33%), $[\alpha]_D$ +10° (*c* 3.7, chloroform); lit.[17] $[\alpha]_D$ +9.8° (chloroform). ^{1}H-N.m.r. data (Me_2SO-d_6): δ 1.0–1.4 (m, 12 H, CMe_2, 2 SCH_2Me), 2.5–2.9 (q, 4 H,

2 SCH_2Me), 3.0–4.5 (m, 6 H), 4.88 (d, 1 H, secondary OH), and 5.07 (d, 1 H, secondary OH).

Further elution with light petroleum–ethyl acetate (4:1) yielded the 3,4-acetal **20** (0.02 g, 1%), $[\alpha]_D$ −26° (*c* 2.3, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.00–1.80 (m, 12 H, CMe_2, 2 SCH_2*Me*), 2.28 (b, 2 H, exchangeable with D_2O, 2 OH), 2.52–3.00 (m, 4 H, SCH_2Me), and 3.52–4.60 (m, 6 H).

Further elution with light petroleum–ethyl acetate (4:1) yielded the 2,4-acetal **22** (0.60 g, 26%), $[\alpha]_D$ −17° (*c* 1, chloroform); lit.[17] $[\alpha]_D$ −16.7° (chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.00–1.80 (m, 12 H, CMe_2, 2 SCH_2*Me*), 2.12 (b, 2 H, exchangeable with D_2O, 2 OH), 2.40–3.20 (m, 4 H, 2 SCH_2Me), and 3.60–4.64 (m, 6 H).

Acetylation reactions. — *(a) 4,5-*O*-Isopropylidene-*D*-ribose diethyl dithioacetal* (**18**). A solution of **18** (0.1 g) in pyridine (10 mL) was treated overnight with acetic anhydride (2 mL). Isolation using chloroform yielded the diacetate **19** (0.12 g, 94%), $[\alpha]_D$ −16° (*c* 2.9, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.0–1.8 (m, 12 H, CMe_2, 2 SCH_2*Me*), 2.00–2.20 (2 s, 6 H, 2 AcO), 2.52–3.00 (q, 4 H, 2 SCH_2Me), 3.60–4.60 (m, 4 H, H-1,4,5,5), 5.36 (dd, 1 H, H-3), and 5.66 (dd, 1 H, H-2).

*(b) 3,4-*O*-Isopropylidene-*D*-ribose diethyl dithioacetal* (**20**). — A solution of **20** (15 mg) in dry pyridine (2 mL) was treated overnight at room temperature with acetic anhydride (1 mL). Isolation using chloroform yielded the diacetate **21** (16 mg, 83%). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.18, 1.35 (2 t, 6 H, 2 SCH_2*Me*), 1.45, 1.54 (2 s, 6 H, CMe_2), 2.15 (s, 6 H, 2 AcO), 2.50–2.90 (q, 4 H, 2 SCH_2Me), 3.80–4.40 (m, 5 H), and 5.34 (t, 1 H, $J_{1,2}$ 10 Hz, H-2).

*(c) 2,4-*O*-Isopropylidene-*D*-ribose diethyl dithioacetal* (**22**). — A solution of **22** (0.20 g) in dry pyridine (5 mL) was treated overnight at room temperature with acetic anhydride (1 mL). Isolation using chloroform yielded the diacetate **23** (0.205 g, 80%). ^{1}H-N.m.r. data (220 MHz, $CDCl_3$): δ 1.20, 1.35 (2 t, 6 H, 2 SCH_2*Me*), 1.44, 1.52 (2 s, 6 H, CMe_2), 2.09 (s, 6 H, 2 AcO), 2.57–2.87 (m, 4 H, 2 SCH_2Me), 3.40–4.40 (m, 5 H), and 5.18 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.5 Hz, H-3).

*2,3:4,5-Di-*O*-isopropylidene-*aldehydo*-D-ribose* (**11**). — The mercaptal **14** (8.5 g) in aqueous acetone was stirred with yellow mercuric oxide (20 g) whilst a solution of mercuric chloride (18 g) in acetone (40 mL) was added dropwise. After stirring overnight, the mixture was filtered through Celite and concentrated *in vacuo*. The residue was extracted with chloroform, the extract was washed with saturated aqueous potassium iodide and then water, dried, and concentrated to yield a mobile liquid (4.6 g). Elution from silica gel with light petroleum–ether (2:1) gave **11** (4.1 g, 70%) $[\alpha]_D$ −17° (*c* 1.1, chloroform); lit.[28] $[\alpha]_D$ −11.8° (chloroform); ν_{max}^{film} 2988, 2938, 1743 (C=O), 1380, 1370 (CMe_2), 1243, 1213, and 1150 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.08–1.64 (m, 12 H, 2 CMe_2), 3.80–4.70 (m, 5 H), and 9.72 (d, 1 H, *J* 2 Hz, CHO).

Anal. Calc. for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.48; H, 7.79.

*2,5:3,4-Di-*O*-isopropylidene-*aldehydo*-D-ribose* (**30**). — The mercaptal **17**

(7.0 g) in acetone (240 mL) and water (60 mL) was stirred with cadmium carbonate (34 g) while a solution of mercuric chloride (34 g) in acetone (120 mL) was added dropwise. After 15 h, the product was isolated using chloroform, yielding a syrup (3.1 g), which was eluted from silica gel with light petroleum–ether (5:3) to yield **30** (2.75 g, 57%), $[\alpha]_D$ −54° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.12–1.60 (m, 12 H, 2 CMe_2), 3.80–4.28 (m, 5 H), and 9.68 (s, 1 H, CHO). Mass spectrum: *m/z* 231 ($M^+ + 1$) weak, 215 ($M^+ - 15$), and 201 ($M^+ - 29$) weak.

*2,3:4,5-Di-*O*-isopropylidene-*D*-ribitol* (**24**). — The aldehyde **11** (2.1 g) in aqueous 50% ethanol (150 mL) was treated with sodium borohydride (3.65 g) for 2.5 h. Isolation using chloroform yielded a syrup, which was eluted from silica gel with light petroleum–ether (7:3) to give **24** (1.3 g, 61%), $[\alpha]_D$ +24° (*c* 1.8, chloroform); lit.[29] $[\alpha]_D$ +7° (ethanol). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.34, 1.38 (2 s, 12 H, 2 CMe_2), 2.68 (bs, 1 H, exchangeable with D_2O, OH), and 3.60–4.44 (m, 7 H).

Anal. Calc. for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.55; H, 8.66.

*2,5:3,4-Di-*O*-isopropylidene-*D*-ribitol* (**25**). — The aldehyde **30** (1.2 g) in aqueous 50% ethanol (100 mL) was treated with sodium borohydride (1.98 g) at room temperature for 2.5 h. The product was then isolated using chloroform, to yield **25** (0.96 g, 79%). Recrystallisation from benzene–light petroleum gave **25**, m.p. 94–100°, $[\alpha]_D$ −84° (*c* 1.1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.30, 1.33, 1.45 (3 s, 12 H, 2 CMe_2), 2.04 (bs, 1 H, exchangeable with D_2O, OH), and 3.40–4.16 (m, 7 H).

Anal. Calc. for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 57.08; H, 8.77.

*1-*O*-Benzoyl-2,3:4,5-di-*O*-isopropylidene-*D*-ribitol* (**28**). — A solution of **24** (0.20 g) in pyridine (5 mL) was treated overnight at room temperature with benzoyl chloride (0.2 mL, 2 mol). Isolation using chloroform yielded **28** (0.24 g, 83%), m.p. 82–83°, $[\alpha]_D$ −33° (*c* 1.3, chloroform); Foster and co-workers[16] reported m.p. 79–80°, $[\alpha]_D$ −32°, for a benzoate prepared by a similar procedure. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.26, 1.34, 1.42 (3 s, 12 H, 2 CMe_2), 3.58–4.80 (m, 7 H), and 7.20–8.12 (m, 5 H, Ph).

Anal. Calc. for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.28; H, 7.14.

*2,3:4,5-Di-*O*-isopropylidene-1-*O*-toluene-*p*-sulphonyl-*D*-ribitol* (**29**). — *(a) Synthesis.* A solution of **24** (0.20 g) in pyridine (4 mL) was stirred overnight with toluene-*p*-sulphonyl chloride (0.328 g, 2 mol). Isolation using chloroform yielded **29**. Recrystallisation from 2-propanol gave **29** (0.305 g, 92%), m.p. 91–92°. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.16, 1.22, 1.24 (3 s, 12 H, 2 CMe_2), 2.31 (s, 3 H, *Me*-Ar), 3.60–4.44 (m, 7 H), 7.20 (d) and 7.69 (d) (4 H, Ar). Mass spectrum: *m/z* 371 ($M^+ - 15$), 295 ($M^+ - 91$), 143 ($M^+ - 243$), and 101 ($Me_2CO_2C_2H_3^+$). The sulphonate was unstable at room temperature and satisfactory analytical data could not be obtained.

Reaction with sodium benzoate. A solution of **29** (0.20 g) in *N,N*-dimethylformamide (10 mL) was heated under reflux for 6 h in the presence of sodium benzoate (0.60 g). Isolation using chloroform yielded a solid residue (0.147 g),

which was eluted from silica gel with light petroleum–ether (17:3) to give the benzoate **28** (0.100 g, 57%), m.p. 82°, identical (t.l.c., i.r. and n.m.r. spectra) with a sample prepared by benzoylation of **24** as described above.

Elution with light petroleum–ether (3:17) then yielded syrupy 1,4-anhydro-2,3-*O*-isopropylidene-D-ribitol (**35**; 36 mg, 40%). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.31, 1.49 (2 s, 6 H, CMe_2), 2.60–2.96 (b, 1 H, exchangeable with D_2O, OH), and 3.48–4.92 (m, 7 H), indistinguishable from that of DL-**35** below. Mass spectrum: *m/z* 159 ($M^+ - 15$) and 143 ($M^+ - 31$).

A solution of **35** (18 mg) in pyridine (2 mL) was treated overnight at room temperature with toluene-*p*-sulphonyl chloride (0.04 g, 2 mol). Isolation using chloroform gave a product which, after recrystallisation from aqueous ethanol, afforded **36** (28 mg, 82%), m.p. 79–81°, $[\alpha]_D$ +14° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.26, 1.42, (2 s, 6 H, CMe_2), 2.38 (s, 3 H, *Me*-Ar), 3.80–4.24 (m, 5 H), 4.52–4.96 (m, 2 H), 7.27, and 7.70 (2 d, 4 H, Ar), indistinguishable from that of DL-**36** below.

Anal. Calc. for $C_{15}H_{20}O_6S$: C, 54.87; H, 6.14; S, 9.75. Found: C, 54.68; H, 6.07; S, 9.69.

(c) Solvolysis. A solution of **29** (0.325 g) in aqueous 50% ethanol (20 mL) was boiled under reflux overnight in the presence of calcium carbonate (1.5 g) and then filtered. The product was isolated using chloroform, yielding a syrup (0.10 g), which was eluted from silica gel with light petroleum–ether (3:17) to give **35** (0.087 g, 61%), identical (t.l.c., i.r. and ^{1}H-n.m.r. spectra) to the sample obtained in *(b)*.

*1,4-Anhydro-2,3-*O*-isopropylidene-5-*O*-toluene-*p*-sulphonyl-*DL*-ribitol* (**36**). — A mixture of 1,4-anhydro-DL-ribitol[30] (0.60 g), acetone (45 mL), conc. sulphuric acid (1.0 mL), and anhydrous copper sulphate (0.4 g) was stirred at room temperature overnight. Isolation using chloroform yielded the DL-acetal **35** as a viscous liquid (0.740 g, 94%). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.31, 1.48 (2 s, 6 H, CMe_2), 2.80 (bs, 1 H, exchangeable with D_2O, OH), and 3.56–4.88 (m, 7 H).

A solution of **35** (0.30 g) in pyridine (3 mL) was treated overnight with toluene-*p*-sulphonyl chloride (0.657 g, 2 mol). Isolation using chloroform yielded **36**. Recrystallisation from ethanol gave **36** (0.462 g, 82%), m.p. 96°. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.27, 1.43 (2 s, 6 H, CMe_2), 2.39 (s, 3 H, *Me*-Ar), 3.68–4.24 (m, 5 H), 4.48–4.92 (m, 2 H), 7.27 (d), and 7.74 (d) (4 H, Ar).

Anal. Calc. for $C_{15}H_{20}O_6S$: C, 54.87; H, 6.14; S, 9.75. Found: C, 54.85; H, 6.34; S, 9.62.

*1-*O*-Benzoyl-2,5:3,4-di-*O*-isopropylidene-*D*-ribitol* (**31**). — A solution of **25** (0.10 g) in dry pyridine (2 mL) was treated with benzoyl chloride (0.13 mL, 2.5 mol) overnight at room temperature. Isolation using chloroform yielded syrupy **31** (0.125 g, 86%), $[\alpha]_D$ −70° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.31, 1.49 (2 s, 12 H, 2 CMe_2), 3.72–4.64 (m, 7 H), and 7.16–8.12 (m, 5 H, Ph).

Anal. Calc. for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.50; H, 7.30.

Isopropylidenation of ribitol (**32**). — A mixture of ribitol (3 g) and dry acetone (60 mL) was stirred overnight with conc. sulphuric acid (0.5 mL) and

anhydrous copper sulphate (6 g). T.l.c. (light petroleum–ethyl acetate, 3:2) then revealed two products [*A* (major) and *B*], R_F 0.77 and 0.42, respectively. The solution was filtered and concentrated to yield a syrup which was eluted from silica gel with light petroleum–ethyl acetate (9:1) to yield fraction *A* (4 g, 87%), which was a mixture of DL-**24** and **33**. ^{1}H-N.m.r. data (Me_2SO-d_6): δ 1.28, 1.36 (2 s, 12 H, 4 CMe_2), 3.60–4.20 (m, 7 H), 4.54 (t, 1 H, exchangeable with D_2O, primary OH), and 5.15 (d, 1 H exchangeable with D_2O, secondary OH).

Further elution yielded fraction *B*, which crystallised on standing, affording DL-**25**. Recrystallisation from ethyl acetate–light petroleum gave material (0.50 g, 11%) with m.p. 105–107°. The ^{1}H- and ^{13}C-n.m.r. spectra were identical with those of 2,5:3,4-di-*O*-isopropylidene-D-ribitol (**25**) described above.

*1-O-Benzoyl-2,3:4,5-di-O-isopropylidene-*DL*-ribitol* (DL-**28**) *and 3-O-benzoyl-1,2:4,5-di-O-isopropylideneribitol* (**34**). — A solution of fraction *A* (2.0 g) in dry pyridine (50 mL) at 0° was treated dropwise with benzoyl chloride (0.5 mL, 0.5 mol) and then kept at room temperature for 2 h. The product was isolated using chloroform, and eluted from silica gel with light petroleum–ether (49:1) to give DL-**28** (0.62 g, 21%), m.p. 71°. The ^{1}H- and ^{13}C-n.m.r. spectra were identical with those of 1-*O*-benzoyl-2,3:4,5-di-*O*-isopropylidene-D-ribitol (**28**) described above. Foster and co-workers[22] reported m.p. 73–74° for the primary benzoate of a product of the isopropylidenation of ribitol.

Further elution with light petroleum–ether (5:1) yielded 1,2:4,5-di-*O*-isopropylideneribitol (**33**; 1.5 g, 75%) as a syrup, a solution of which in dry pyridine (40 mL) was treated dropwise with benzoyl chloride (1.5 mL, 2 mol) at 0°, followed by heating at 100° for 1 h. Isolation using chloroform yielded **34** which, after recrystallisation from aqueous pyridine, had m.p. 69–71°; lit.[22] m.p. 69–71°. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.40 (s, 12 H, 4 CMe_2), 4.10–4.56 (m, 6 H), 5.51 (t, 1 H, *J* 4 Hz, H-3), and 7.34–8.26 (m, 5 H, Ph).

*Reaction of 2,3:4,5-di-*O*-isopropylidene-*aldehydo-D-*ribose* (**11**) *with ethynylmagnesium bromide.* — Ethylmagnesium bromide [from magnesium (4 g) and ethyl bromide (15.5 g)] in dry tetrahydrofuran (130 mL) was added dropwise to tetrahydrofuran (200 mL) saturated with acetylene, with passage of acetylene throughout. After the addition of ethylmagnesium bromide was complete, the addition of acetylene was continued for a further 1.5 h. A solution of **11** (5 g) in dry tetrahydrofuran (100 mL) was then added dropwise with passage of acetylene throughout and then for a further 2 h. The solution was then concentrated (to ~100 mL) and ether (200 mL) was added. The ether extract was washed with aqueous 10% ammonium chloride (3 × 200 mL) and then water, dried (Na_2SO_4), and filtered through charcoal–Celite, and concentration *in vacuo* yielded a syrupy mixture (4.5 g, 81%) of **39** and **40**. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.20–1.80 (m, 12 H, 2 CMe_2), 2.32 (bs, 1 H, exchangeable with D_2O, OH), 2.46 (d, 1 H, C≡CH), and 3.60–4.40 (m, 6 H). Mass spectrum: *m/z* 256 (M^+) and 241 ($M^+ - 15$).

A solution of the mixture (1 g) in pyridine (10 mL) was treated overnight at room temperature with acetic anhydride (2 mL). Isolation using chloroform yielded

a mixture (1.1 g, 95%) of the monoacetates **41** and **42**. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.20–1.60 (m, 12 H, 4 CMe_2), 2.08, 2.10 (2 s, 3 H, 2 AcO), 2.40 (d, 1 H, C≡CH), 3.60–4.20 (m, 5 H), and 5.56–5.70 (m, 1 H, H-3,3): δ 2.08 and 2.10 were in the ratio ~1:2.

2,3-O-Isopropylidene-β-D-ribofuranosylethyne (**45**) *and 2,3-O-isopropylidene-α-D-ribofuranosylethyne* (**46**). — A solution of the above mixture (2.5 g) of **39** and **40** in pyridine (100 mL) was treated overnight at room temperature with toluene-*p*-sulphonyl chloride (3 g). Isolation using chloroform yielded a mixture of sulphonates **43** and **44** (3.0 g, 70%). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.20–1.80 (m, 12 H, 2 CMe_2), 2.36 (d, 1 H, C≡CH), 2.42 (s, 3 H, *Me*-Ar), 3.60–4.80 (m, 5 H), 5.36 (m, 1 H, H-3), and 7.32–7.84 (4 H, Ar). A solution of this mixture (3.0 g) in aqueous 50% ethanol (25 mL) containing calcium carbonate (8 g) was boiled under reflux for 72 h, filtered, and concentrated to dryness. The residue was eluted from silica gel with light petroleum–ethyl acetate (9:1) to give **45** (0.90 g, 60%), $[\alpha]_D$ −21° (*c* 2, chloroform); lit.[31] $[\alpha]_D$ −21.1° (chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.32, 1.48 (2 s, 6 H, CMe_2), 2.40–2.68 (bs, 1 H, OH), 2.56 (d, 1 H, C≡CH), and 3.60–4.70 (m, 6 H). Mass spectrum: *m/z* 199 (m) ($M^+ + 1$), 198 (w) (M^+), and 183 (s) ($M^+ - Me$).

Further elution yielded **46** (0.40 g, 27%), $[\alpha]_D$ −48° (*c* 2, chloroform); lit.[12] $[\alpha]_D$ −48.3° (chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.28, 1.48 (2 s, 6 H, CMe_2), 1.80 (bs, 1 H, OH), 2.40 (d, 1 H, C≡CH) 3.50–3.80 (m, 2 H), 4.05 (t, 1 H), and 4.55–4.80 (m, 3 H).

β-D-Ribofuranosylethyne (**47**). — A solution of **45** (0.70 g) in aqueous 50% methanol (20 mL) was heated under reflux for 2 h with Amberlite IR-120 (H^+) resin (0.90 g). Filtration and concentration then yielded a syrup which crystallised from ethyl acetate–light petroleum to give **47** (0.30 g, 54%), m.p. 64–65°, $[\alpha]_D$ −18° (*c* 0.7, methanol); lit.[31] m.p. 63–64°, $[\alpha]_D$ −18.2° (methanol). The identity of these compounds was confirmed by comparison of their i.r. spectra.

α-D-Ribofuranosylethyne (**48**). — A solution of **46** (0.40 g) in aqueous 50% methanol (20 mL) was heated at 90° for 4 h with Amberlite IR-120 (H^+) resin (0.90 g). Filtration and concentration then yielded a syrup which crystallised from ethyl acetate to give **48** (0.15 g, 48%), m.p. 100–101°, $[\alpha]_D$ +4° (*c* 1.2, methanol); lit.[31] m.p. 99–100°, $[\alpha]_D$ +6.3° (methanol). The identity of these compounds was confirmed by comparison of their i.r. spectra.

ACKNOWLEDGMENT

We thank Dr. I. H. Sadler and his colleagues at Edinburgh University for the ^{13}C-n.m.r. spectra.

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