CONFIGURATIONAL AND CONFORMATIONAL STUDIES ON SOME BENZYLIDENE DERIVATIVES OF D-RIBOSE AND DI-β-D-RIBOFURANOSE 1,5':1',5-DIANHYDRIDE

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ABSTRACT

Benzylidenation of D-ribose under diverse conditions yields a variety of products, most of which are formed as mixtures of diastereoisomers. The conformations assumed by the furanose rings in the 2,3-O-benzylidene- β -D-ribose derivatives are discussed in relation to the coupling constants obtained by comparing the experimental and computed n.m.r. spectra.

INTRODUCTION

It is well known that acid-catalyzed benzylidenation of *vic*-diols, at room temperature and above, yields mixtures of the two diastereoisomeric 2-phenyl-1,3-dioxolane derivatives¹. Treatment of D-ribose with benzaldehyde and an acid catalyst under various conditions has given a variety of products; different physical constants have frequently been reported²⁻⁴ for the "same product" prepared under different conditions. In connection with some work on a dianhydride of D-ribose⁵, the benzylidenation of D-ribose under diverse conditions was re-examined, and we report now the results of this study.

RESULTS AND DISCUSSION

When D-ribose was shaken with benzaldehyde, zinc chloride, and glacial acetic acid for 24 h at 5°², 2,3-O-benzylidene- β -D-ribofuranose was obtained as a mixture of diastereoisomers (1a and 2a) in 48% yield. The n.m.r. spectrum of this product showed an approximately 1-proton singlet at τ 4.23 and a very weak singlet at τ 4.05, attributable to benzylidene-methine protons⁶. These signals have been assigned, respectively, to the structure 1a having the benzylidene-methine proton *exo* (*syn* isomer) and to the structure 2a having this proton *endo* (*anti* isomer); it has been found⁷ in several 2-substituted 1,3-dioxolanes that the *syn* (or *cis*) isomer displays an upfield chemical shift for the C-2 proton in comparison with the *anti* (or *trans*) isomer.

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Although traces of the *anti* isomer (2a) could not be removed by repeated recrystallization from benzene, the *syn* isomer (1a) could be obtained by preparation of the crystalline 1,5-diacetate (1b), followed by de-O-acetylation to give pure 1a. The n.m.r. spectrum of 1a in acetone- d_6 containing 1 drop of deuterium oxide showed a 1-proton singlet at τ 4.68 for the anomeric proton, which confirms⁸ a *trans* relationship between the protons on C-1 and C-2 of the ribofuranose ring and that the hydroxyl group on C-1 has the β configuration.



Treatment of D-ribose with benzaldehyde, zinc chloride, and glacial acetic acid for 24 h at 27° gave a mixture of three components, which could be separated by a procedure involving chromatography on alumina and silica gel. The n.m.r. spectrum of the major component showed that it was a mixture of di-O-benzylidene-D-ribose derivatives. This component melted at 89-91° and had a specific optical rotation of + 1.5°. Barker and Spoors³ reported the isolation of a 1,5:2,3-di-O-benzylidene- β -Dribofuranose having a m.p. of $117-119^{\circ}$ and a specific optical rotation of $+7.3^{\circ}$ from a reaction mixture, in which D-ribose had been shaken, with benzaldehyde and zinc chloride only, for 20 h at 18°. A second component, isolated from the reaction performed at 27°, was obtained in low yield (3%), and was shown to be an approximately 1:1 mixture of the diastereoisomers (1a and 2a) of 2,3-O-benzylidene- β -Dribofuranose. The anti isomer (2a) could be separated from the syn isomer (1a) by acetylating the mixture and separating the diacetates (1b and 2b) by silica gel chromatography; de-O-acetylation of 2b gave the pure anti isomer (2a) of 2,3-O-benzylidene- β -D-ribofuranose with the benzylidene-methine proton endo (τ 4.05). The n.m.r. spectrum of 2a, which showed a 1-proton singlet at τ 4.57 for the anomeric proton, confirms⁸ that there is a trans relationship between the protons on C-1 and C-2 of the D-ribofuranose ring and that the hydroxyl group on C-1 has the β configuration. The third component, isolated from the reaction performed at 27°, was obtained in crystalline form and gave an analysis consistent with a monobenzylidene derivative

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of D-ribose. The structure of 1,2-O-benzylidene- α -D-ribofuranose has been tentatively assigned to this compound. The compound did not react with periodate, and its n.m.r. spectrum in chloroform-d showed for H-1 a doublet with a spacing of 4.0 Hz, a value in the range observed⁹ for the coupling constants of the bridgehead hydrogen atoms (H-1 and H-2) in 1,2-cis-fused ring systems of several glycofuranoses. It is interesting that the n.m.r. spectrum did not show the presence of two diastereoisomers; only one signal was observed attributable to a benzylidene-methine proton.

When D-ribose is heated with benzaldehyde, zinc chloride, and glacial acetic acid for 1 h at $80^{\circ 2}$, the major component produced is a di-O-benzylidene derivative of a dianhydride of D-ribose. The structure of the parent dianhydride has been established⁵ to be that of di- β -D-ribofuranose 1,5':1',5-dianhydride; this compound can be obtained^{2,5} by catalytic de-O-benzylidenation of the di-O-benzylidene derivative formed at 80°. For di-(2,3-O-benzylidene- β -D-ribofuranose) 1,5':1',5-dianhydride, three diastereoisomers are possible, namely, the two with both benzylidenemethine protons either endo (3) or exo (4), and that with one benzylidene-methine proton endo and the other exo. The n.m.r. spectrum in chloroform-d of the product obtained in the present work showed two singlets at τ 4.05 and τ 4.25, whose integration corresponded to two protons in a ratio of approximately 3:2. These signals are assigned to endo and exo benzylidene-methine protons, respectively. The crystalline product is clearly a mixture of diastereoisomers. Although this mixture was not resolved in t.l.c., the diastereoisomer having both benzylidene-methine protons exo (4) could be prepared almost pure, when the benzylidenation was performed on di- β -Dribofuranose 1,5':1',5-dianhydride⁵ for 24 h at 5°; the n.m.r. spectrum in chloroform-d showed a 2-proton singlet at τ 4.25 for the exo benzylidene-methine protons and only a small absorption at τ 4.07 for the *endo* protons.

Examination by t.l.c. of the mother liquors from the crystallization of the di-(2,3-O-benzylidene- β -D-ribofuranose) 1,5':1',5-dianhydride showed the presence of two major components, and trace amounts of this dimer and the two diastereoisomers of 2,3-O-benzylidene- β -D-ribofuranose. The two major components were isolated by column chromatography. The n.m.r. spectrum of one of them was identical with that of the *syn* isomer (5) of 1,5-anhydro-2,3-O-benzylidene- β -D-ribofuranose, a sample of which was prepared from *syn*-2,3-O-benzylidene- β -D-ribofuranose (1a) by way of the 5-O-p-tolylsulfonyl derivative by the method of Vis and Fletcher⁴. The n.m.r. and i.r. spectra of the other major component were similar to those of the *syn* isomer (5) of 1,5-anhydro-2,3-O-benzylidene- β -D-ribofuranose, and the compound is, presumably, the *anti* isomer (6). In each of the n.m.r. spectra of the two components, the H-1 signal was a singlet, an observation consistent with the β -D configuration for the group on C-1 and hence confirming the assignment of the β -D configuration in the case of the 2,3-O-benzylidene-D-ribofuranoses and their 1,5-diacetates.

The results of the present study show that it is possible to obtain almost pure diastereoisomers of 2,3-O-benzylidene- β -D-ribofuranose (1a) and di-(2,3-O-benzylidene- β -D-ribofuranose) 1,5':1',5-dianhydride (4) with the benzylidene-methine protons exo (syn isomers) by performing the benzylidenation reactions at 5° (cf. ref. 10).

At room temperature and above, equilibration of the *anti* isomer with the initially formed *syn* isomer occurs to give an approximately equimolar mixture of the two diastereoisomers. In an investigation of the configurational stability of 2,4-*cis*-5-trisubstituted 1,3-dioxolanes, Eliel *et al.*^{1,7} showed that the *syn* isomers are generally thermodynamically more stable than the *anti* isomers, unless the substituents are large; thus, for example, the *syn* isomer of 2,4-*cis*-5-trimethyl-1,3-dioxolane predominates over the *anti* isomer at equilibrium. Some data for the individual diastereoisomers of the 2,3-O-benzylidene- β -D-ribose derivatives prepared in the present work are summarized in Table I. It is notable that the *syn* isomers **1a** and **1b** have lower algebraic values for their specific optical rotations than have their respective *anti* isomers **2a** and **2b**; this observation is also characteristic of the 2,3-O-benzylidene derivatives of adenosine reported earlier¹⁰.

TABLE I

Chemical shifts of benzylidene-methine protons, specific optical rotations, and melting points of 2,3-O-benzylidene-d-ribose derivatives

Compound	Configuration of benzylidene-methine proton(s)	Chemical shift (τ) ^a of benzylidene-methine proton	[α] ²³ (°)	<i>M.p.</i> (°)	
1a	exo	4.23 ^b	-27.8 (CH ₃ OH)	125-126	
2 a	endo	4.05	-14.0 (CH ₃ OH)	107-108	
1b	exo	4.21 ^c	-68.8 (CHCl ₁)	78–79	
2b	endo	3.99°	-44.1 (CHCl ₃)	Syrup	
4	exo	4.25 ^c	-42.1 (CHCl ₃)	209-210	
5	exo	4.32°	-51.5 (CHCl ₃) ^d	140-170 ^d	
б	endo	3.84°	- 55.7 (CHCl ₃)	106107	

^aN.m.r. spectra recorded at 60 MHz. ^bAcetone- d_6 containing 1 drop of D₂O. ^cChloroform-d. ^dCompound 5 slightly contaminated with di-(2,3-O-benzylidene- β -D-ribofuranose) 1,5':1',5-dianhydride.

The n.m.r. spectra of the 2,3-O-benzylidene- β -D-ribose derivatives prepared in the present work were analyzed as ABCDE systems (for H-2, 3, 4, 5, and 5') or slightly simpler patterns by use of the Laocoon II program of Castellano and Bothner-By¹¹, and the results are given in Tables II and III. For this series of compounds, the magnitudes of the couplings between H-1 and H-2 are small (<0.5 Hz), as are those between H-3 and H-4 (<1.5 Hz); the magnitudes of the couplings between H-2 and H-3 are either large (~6 Hz), or unobservable (and presumably large) because of accidental equivalence of chemical shifts. These couplings suggest¹² that the most important contributors to the conformational equilibria have dihedral angles of 60–120° between H-1 and H-2* and between H-3 and H-4, and of 25–50° between H-2 and H-3.

^{*}The magnitude of the coupling between H-1 and H-2 is diminished by the additional electronegative substituent, so that an approximately zero coupling constant is less accurate as a guide for the dihedral angle.

BENZYLIDENE DERIVATIVES

TABLE II

CHEMICAL-SHIFT DATA	(60 MHz) FOR 2,3	-O-BENZYLIDENE-D-RIBOSE	DERIVATIVES
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Compound	Chemical shifts (t)							
	H-1	H-2	H-3	H-4	H-5	H-5'		
 1a ^a	4.58	5.37	5.11	5.61	6.33	6.33		
2aª	4.57	5.37	5.01	5.63	6.30	6.30		
l b°	3.64	5.22	5.22	5.40	5.84	5.84		
2.b ^b	3.62	5.19	5.13	5.43	5.82	5.82		
1 ⁶	4.80	5.40	5.09	5.54	6.15	6.28		
56	4.38	5.64	5.64	5.15	6.71	6.56		
56	4.40	5.51	5.51	5.13	6.63	6.59		
5- <i>O-p</i> -Tolylsulfonyl derivative of 1 a ^{a,c}	4.43	5.33	5.25	5.51	5.82	5.82		

^aAcetone- d_6 containing 1 drop of D₂O. ^bChloroform-*d*. ^cThe chemical shift of the *exo* benzylidenemethine proton in this compound is τ 4.23.

TABLE III

COUPLING	CONSTANTS	FOR 2,3-0)-BENZYLIDENE-D	-RIBOSE	DERIVATIV	ES
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Compound	Coupling constants (Hz)							
	J _{1,2}	J _{2,3}	J _{3,4}	J4,5		J _{4,5} ,	J _{5,5} ,	
1a ^a	<0.5	6.1	0.8		8.5°		đ	
2a ^a	<0.5	5.6	1.3		8.2 ^c		đ	
1b ^b	<0.5	đ	< 0.5		13.4 ^c		đ	
2b ^b	<0.5	5.9	<0.5		13.7°		đ	
<u>4</u> ^b	<0.5	6.5	0.8	1.8		1.6	11.4	
5 ^b	<0.5	đ	<0.5	0.2		3.8	7.5	
- 6 ^b	< 0.5	đ	< 0.5	0.3		4.0	7.5	
5-O-p-Tolylsulfonyl derivative of 1a ^a	<0.5	6.2	1.1		13.4°		đ	

^{*a,b*}See footnotes ^{*a*} and ^{*b*} in Table II. ${}^{c}J_{4,5} + J_{4,5}$. ^{*d*}Unobservable because of accidental equivalence of chemical shifts.

X-Ray crystallographic studies¹³ on some 1-substituted β -D-ribofuranose derivatives have indicated conformations with puckering only at C-2 or C-3 in the furanoid ring. In solution, furanoid¹⁴ and 1,3-dioxolane¹⁵ rings exist as rapidly pseudorotating mixtures with very small energy barriers between the conformers; however, substituents can impose restrictions on the pseudorotational itineraries. The dihedral angles suggested for the fused ring systems in the present work are consistent with conformations of the furanoid ring having the ring oxygen atom displaced below and C-1 or C-4 displaced above the plane of the ring. The ¹T_o and ⁴T_o conformations are probably the major contributors, although ¹E and ⁴E conformations may also be present. The conformation at the mid-point of this limited itinerary, E_0 , is probably of little importance, because it would require eclipsing of two oxygen atoms. Conformations having C-2 or C-3 out of the plane of the furanoid ring are also relatively unimportant.

EXPERIMENTAL

General. — Melting points were determined on a Fisher–Johns melting-point apparatus and are uncorrected. Microdistillations were performed with a Gallenkamp heating block. Optical rotations were measured with a Perkin–Elmer Model 141 automatic polarimeter at 23 $\pm 2^{\circ}$. I.r. spectra were recorded with a Beckman IR5A spectrophotometer. N.m.r. spectra were recorded at 60 MHz in chloroform-*d* or acetone- d_6 with tetramethylsilane as the internal standard; theoretical spectra were calculated with an IBM 360 computer, equipped with a CALCOMP plotter, by use of a modification of the Laocoon II program of Castellano and Bothner-By¹¹. T.l.c. was performed with Silica Gel G as the adsorbent; the developed plates were air-dried, sprayed with 5% ethanolic sulfuric acid, and heated at about 150°. The term "petroleum ether" refers to the fraction of b.p. 60–80°.

Benzylidenations were performed by shaking together the substrate and reagents under the specified conditions. The reaction mixture was poured into ice-water, and the mixture was extracted three times with ether. The combined ether extracts were washed with water and sodium hydrogen carbonate solution, dried over anhydrous magnesium sulfate, and concentrated to dryness.

Benzylidenation of D-ribose at 5°. — D-Ribose (5.0 g) was treated with benzaldehyde, zinc chloride, and glacial acetic acid at 5° as described by Wood *et al.*² to give a crystalline product (**1a** and **2a**, 3.8 g, 48%); m.p. 120–121°; $[\alpha]_D^{23} - 26.6^\circ$ (*c* 1.02, methanol), -25.6° (*c* 0.98, chloroform); λ_{max}^{Nujol} 3.1 (OH), 13.1, 14.3 μ m (Ph); n.m.r. data in acetone- d_6 containing 1 drop of D₂O: τ 4.23 (~1-proton singlet, *exo* benzylidene-methine H), 4.05 (trace of *endo* benzylidene-methine H); lit.²: m.p. 123– 124° and $[\alpha]_D^{20} - 26.6^\circ$ (*c* 0.6, methanol), -22.4° (*c* 1,4. chloroform).

syn-1,5-Di-O-acetyl-2,3-O-benzylidene- β -D-ribofuranose (1b). — A portion (407 mg) of the product obtained from the preceding experiment was treated with dry pyridine (6 ml) and acetic anhydride (5 ml) at room temp. After 16 h, the reaction mixture was poured into ice-water (100 ml); the precipitate was removed by filtration, after 1 h, and recrystallized from ethanol to give needles (379 mg, 69%); m.p. 78–79°, $[\alpha]_{D}^{23} - 68.8^{\circ}$ (c 1.82, chloroform); λ_{max}^{Nujol} 5.73 μ m (OAc), no absorption attributable to OH; n.m.r. data in chloroform-d (see also Tables I, II, and III): τ 2.47–2.62 (5-proton multiplet, Ph group), 8.07 (6-proton singlet, OAc groups on C-1 and C-5).

Anal. Calc. for C₁₆H₁₈O₇: C, 59.6; H, 5.6. Found: C, 59.7; H, 5.7.

syn-2,3-O-Benzylidene- β -D-ribofuranose (1a). — The 1,5-diacetate 1b (193 mg) was dissolved in methanol (10 ml) and 1 drop of a 7% (w/v) solution of sodium in methanol was added. The course of the reaction was followed by t.l.c. (19:1, v/v, chloroform-methanol) and appeared to be complete after 2 h. Dry ice was added to the methanolic solution after 4 h, the solution was filtered, and the filtrate was concentrated to a crystalline product (101 mg, 71%). Three recrystallizations from benzene gave crystals, m.p. 125–126°, $[\alpha]_D^{23} - 27.8^\circ$ (c 1.01, methanol).

Benzylidenation of D-ribose at 27° . — A mixture of D-ribose (5 g), zinc chloride (2.5 g), benzaldehyde (30 ml), and glacial acetic acid (2 ml) was shaken for 24 h at 27° .

T.l.c. (3:2, v/v, ethyl acetate-petroleum ether) of the resultant syrupy product showed the presence of three components having R_F values of 0.98, 0.36, and 0.13. The mixture was dissolved in ether (50 ml) and applied to a column (20 × 2 cm) of alumina (neutral, Brockman Activity 1, mesh 80–200). Elution with ether gave in crystalline form the component having R_F 0.98. Elution with methanol and removal of the solvent yielded a syrupy mixture of the two slower-moving components; these were separated on a column (45 × 2 cm) of silica gel with 3:2 (v/v) ethyl acetate-petroleum ether as eluant.

The component having $R_F 0.98$ was identified as a mixture of di-O-benzylidene-D-ribose derivatives (2.56 g, 23%); m.p. 89–91°, $[\alpha]_D^{23} + 1.5°$ (c 1.36, chloroform); λ_{\max}^{Nujol} 13.1, 13.2, 14.2, 14.3 μ m (Ph), no absorption attributable to OH; n.m.r. data in chloroform-d: τ 2.38–2.87 (10-proton multiplet, 2 Ph groups), 3.93–4.42 (3 protons, 2 benzylidene-methine protons and H-1), 5.12–5.50 (3-protons, H-2, H-3, and H-4), 5.98–6.65 (2-proton broadened quartet, 2 H-5).

The component having $R_{\rm F}$ 0.36 isolated from the benzylidenation reaction at 27° was identified as a mixture of the two diastereoisomers (1a and 2a) of 2.3-Obenzylidene- β -D-ribofuranose, yield 246 mg (3%). This component was crystallized from ethyl acetate-petroleum ether and had m.p. 98-99°; n.m.r. data in acetone- d_6 containing 1 drop of D₂O: τ 4.05 (endo benzylidene-methine H), 4.25 (exo benzylidenemethine H). A portion (98 mg) of the mixture of diastereoisomers was acetylated in the usual manner with acetic anhydride (5 ml) and dry pyridine (6 ml) to give a syrupy product (100 mg, 76%), which was shown by t.l.c. (1:3, v/v, ethyl acetate-petroleum ether) to contain two components having R_F values of 0.17 and 0.29; these were separated on a column $(22 \times 2 \text{ cm})$ of silica gel, with the same solvent as used for t.l.c. as eluant, to give the diacetates 1b and 2b. Compound 1b was obtained crystalline (36 mg) after evaporation of the solvent, and it was revcaled as one spot (R_F 0.52) in t.l.c. (2:3, v/v, ethyl acetate-petroleum ether) corresponding to syn-1,5-di-O-acetyl-2,3-O-benzylidene- β -D-ribofuranose. Compound **2b** (58 mg) was obtained after evaporation of the solvent to leave a syrup, followed by distillation of the syrup at 0.015 torr and collection of the fraction distilling between 150–160°. This fraction was revealed as one spot ($R_F 0.62$) in t.l.c. (2:3, v/v, ethyl acetate-petroleum ether) and had $[\alpha]_D^{23} - 44.1^\circ (c 2.90, \text{ chloroform}); \lambda_{\max}^{CHCl_3} 5.73 \,\mu\text{m}$ (OAc), no absorption attributable to OH; n.m.r. data in chloroform-d (see also Tables I, II and III): 7 2.36-2.62 (5-proton multiplet, Ph group), 7.91 (6-proton singlet, OAc groups on C-1 and C-5). Compound 2b (40 mg) was de-O-acetylated in the usual manner to afford anti-2,3-Obenzylidene-*B*-D-ribofuranose (2a, 29 mg, 95%). Two recrystallizations from ethyl acetate-petroleum ether gave needle-shaped crystals, m.p. 107-108°, $[\alpha]_{D}^{23}$ -14.0° (c 1.15, methanol); R_F 0.44 (t.l.c. in 2:3, v/v, ethyl acetate-petroleum ether); λ_{max}^{Nujol} 3.1 (OH), 13.1, 14.3 μ m (Ph); n.m.r. data in acetone- d_6 containing 1 drop of D₂O: τ 2.40–2.75 (5-proton multiplet, Ph group).

The component having R_F 0.13 (85 mg), isolated from the benzylidenation reaction at 27°, was tentatively assigned the structure of 1,2-O-benzylidene- α -D-ribo-furanose. This component was crystallized from ethyl acetate-petroleum ether, m.p.

92–93°; $[\alpha]_D^{23} + 36.4^\circ$ (c 1.05, chloroform); λ_{max}^{Nujol} 2.92 (OH), 13.2, 14.4 μ m (Ph); n.m.r. data in chloroform-d: τ 2.45–2.82 (5-proton multiplet, Ph group), 3.85 (1-proton singlet, benzylidene-methine H), 4.12 (1-proton doublet, $J_{1,2}$ 4.0 Hz, H-1). A periodate oxidation determination was performed in the following manner. The compound (0.3 mg) was dissolved in a buffer solution (5 ml, 0.2M acetic acid, 0.1M lithium acetate), and sodium metaperiodate (0.428 mg) in the buffer solution (5 ml) was added. Even after 48 h, at either 4° or 35°, an uptake of periodate could not be detected by a polarographic technique¹⁶.

Anal. Calc. for C₁₂H₁₄O₅: C, 60.5; H, 5.9. Found: C, 60.8; H, 6.0.

Benzylidenation of D-ribose at 80°. — Benzylidenation of D-ribose (10 g) at 80° according to the method of Wood et al.² afforded di-(2,3-O-benzylidene- β -D-ribofuranose) 1,5':1',5-dianhydride. The product was recrystallized from acetone (5.4 g, 37%), m.p. 198–200°, $[\alpha]_D^{23}$ – 38.5° (c 1.20, chloroform); λ_{max}^{Nujol} 13.1, 14.4 μ m (Ph), no absorption attributable to OH; n.m.r. data in chloroform-d: $\tau 2.42-2.82$ (10proton multiplet, Ph groups), 4.05, 4.25 (2 singlets corresponding in intensity to 2 protons, endo and exo benzylidene-methine protons, respectively, in the approximate proportion, 3:2). T.l.c. (1:1, v/v, ethyl acetate-petroleum ether) of the mother liquors showed the presence of trace amounts of di- $(2,3-O-benzylidene-\beta-D-ribofuranose)$ 1,5':1',5-dianhydride and of the two diastereoisomers of 2,3-O-benzylidene- β -Dribofuranose, in addition to two major components having R_F values of 0.78 and 0.67. Chromatography on a column $(45 \times 2 \text{ cm})$ of silica gel, with 1:3 ethyl acetate-petroleum ether as eluant, afforded the component having R_F 0.78 slightly contaminated with di-(2,3-O-benzylidene- β -D-ribofuranose) 1,5':1',5-dianhydride, and the component having $R_F 0.67$ in a homogeneous state. The fraction consisting predominantly of the component having R_F 0.78 was obtained crystalline (137 mg), m.p. 140–170°, $\left[\alpha\right]_{D}^{2^{3}}$ - 51.5° (c 1.05, chloroform). Its n.m.r. spectrum in chloroform-d was identical, except for very minor peaks attributable to the contaminant, with that of an authentic sample of the syn isomer (5) of 1,5-anhydro-2,3-O-benzylidene- β -D-ribofuranose [prepared from syn-2,3-O-benzylidene- β -D-ribofuranose (1a) by the method of Vis and Fletcher⁴]. The component having R_F 0.67 was also obtained crystalline, m.p. 106–107°, $[\alpha]_{D}^{23}$ – 55.7° (c 0.70, chloroform); λ_{max}^{Nujol} 13.1, 13.4 µm (Ph), no absorption attributable to OH; n.m.r. data in chloroform-d (see also Tables I, II, and III): $\tau 2.52$ -2.68 (5-proton multiplet, Ph group). This compound was assigned the structure of the anti isomer (6) of 1,5-anhydro-2,3-O-benzylidene- β -D-ribofuranose.

Di-(syn-2,3-O-benzylidene- β -D-ribofuranose) 1,5':1',5-dianhydride (4). — A mixture of di- β -D-ribofuranose 1,5':1',5-dianhydride⁵ (300 mg), zinc chloride (200 mg), benzaldchyde (6 ml), and glacial acetic acid (0.4 ml) was shaken for 24 h at 5°. The resultant product was recrystallized from acetone (53 mg, 10%), m.p. 209–210°, $[\alpha]_D^{23}$ -42.1° (c 0.48, chloroform); λ_{max}^{Nuiol} 13.1, 14.4 μ m (Ph), no absorption attributable to OH; n.m.r. data in chloroform-d (see also Tables I, II, and III): τ 2.34–2.85 (10-proton multiplet, Ph groups), 4.07 (trace of *endo* benzylidene-methine protons), 4.25 (2-proton singlet, *exo* benzylidene-methine protons).

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